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TEXTILE RESEARCH JOURNAL

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Crease Recovery of Fabrics

Part I: Some Tensile Properties of Wool, Vicara, and Rayon Fibers and Their Relationship to Fabric Crease Recovery

John F. Krasny[1] and Arnold M. Sookne[1]

Abstract

A study has been made of some single fiber properties of wool, rayon, and Vicara zein fibers at various relative humidities, and the crease recoveries of fabrics made from the same fibers have been measured under identical conditions. In general, the wool and Vicara are similar in many load-extension properties. A fair correlation was found between fabric crease recovery on the one hand, and fiber tensile and work recovery on the other hand at low and normal humidities. At high humidity, and particularly with wet fabrics, however, this relationship no longer holds. A general correlation also seems to exist between fabric crease recovery and work returned by stretched fibers during retraction from extension to 4%.

Introduction

There are three broad groups of fabric parameters which affect the crease recovery of fabrics: (1) the physical properties of the fiber, (2) fabric construction and history, and (3) finish. Part I of this paper is concerned with some specific aspects of the first point, and Part II deals with the effect of fabric construction on crease recovery.

The literature provides numerous valuable studies of the relationships among fabric structure, fiber properties, and fabric crease recovery and hand. A basic approach to the problem of assaying the contribution of a new fiber to fabric properties such as crease resistance, hand, and drape has been published by Lewis [11], among others. Fiber stress-strain behavior has been thoroughly investigated by several workers, some of whom have attempted to determine those fiber parameters which correlate with fabric properties such as hand and crease recovery. Valuable empirical approaches to this problem have been made by Beste and Hoffman [2, 9] and by Grundfest and Gagliardi [7]. Buck and McCord conducted a broad survey of the various aspects of crease resistance [3], and Hamburger et al. [8] and Sommer [14] have published theoretical considerations concerning the behavior of fibers in creased fabrics. Hamburger has also made a systematic investigation of the effect of yarn and fabric construction parameters on the crease recovery of fabrics made from acetate filament and staple yarns [8]. Gantz [6] and Beste and Hoffman [2] reported data on the effect of humidity on crease recovery and fiber properties. Quantitative data on the effect of storage, laundering, dry cleaning, and wear on the crease recovery of fabrics have been reported only rather recently [5, 13]. A complete survey of the literature on all aspects of crease and wrinkle recovery including test methods, time-recovery relationship, and some information on the effect of chemical finishes can be found in Kaswell's book [10].

The present work was undertaken in order to shed more light on the dependency of crease recov-

[1] Harris Research Laboratories, Inc., Washington, D. C.

ery on fiber properties at relative humidities ranging from 10% to the wet state, and includes results for a fiber, Vicara,[2] for which few data have been heretofore available. Wool, rayon, and Vicara fabrics were included in the investigation; however, no attempt was made to use fabrics of similar construction. The fibers tested were taken from the warps of the fabrics.

Materials

The fabrics used in this investigation were:

1. Wool flannel, 6 oz/sq yd, unfinished except for scouring, average fiber denier 6.1.
2. Viscose rayon lining twill, 4 oz/sq yd, unfinished, bright filament yarns, average filament denier 3.9.
3. Vicara[3] filter fabric, 14 oz/sq yd, unfinished shrinkproof type fibers, 3-ply staple yarns, average fiber denier 3.4, Fiber Code 700 of 1951, dull.
4. Vicara[3] suiting, 8 oz/sq yd, 95% bright Vicara, 5% wool, handwoven in plain weave, average fiber denier (Vicara) 3.8.

Test Methods

All fiber and fabric measurements were conducted at 10, 65, and 95% relative humidity and in the wet state. The fibers studied were in each case removed from the warp yarns of the fabrics and their denier was determined by means of a quartz needle weighing device [12].

The fiber stress-strain properties were determined on an autographic strain gage extensometer patterned after the one described by Dart and Petersen [4]. The fiber length was 1 in., the rate of extension and retraction 30% per min. The fibers were extended successively to 4, 6, 10, and 20%, then to break. After each extension was reached the machine was reversed immediately, and the fiber permitted to retract until a zero load was registered by the strain gage; then extension was again started without delay. The areas under the extension and retraction branches of the load-elongation curves were obtained by integration and converted to work to stretch and work recovered in ergs per cubic centimeter. The ratio of the work recovered during contraction to the work required for extension was calculated and is shown under "work recovery" in Table I. The tensile recovery is the percentage of extension which is recovered during retraction.[4] The compliance ratio is defined by Beste and Hoffman [2] as follows:

$$\text{Compliance ratio} = \frac{(X_1/L_1) - (X_2/L_2)}{X_1 - X_2}$$

where L_1 represents the load at X_1% extension and L_2 the load at X_2% extension. In this work, the values chosen were 10% extension for X_1 and 4% extension for X_2. The physical significance of the compliance ratio is discussed in detail in [2]. It is related to the ability of a fabric to yield when it is compressed manually; this ability, the "give," is believed to be one of the properties which contributes to the "hand" of fabrics. A high compliance ratio, like that of wool, generally corresponds to a "good" hand. Young's modulus, a measure of the slope of the initial portion of the load-elongation curve of a fiber, was also calculated. This is an indication of the fiber stiffness which seems to be reflected in both fabric stiffness and liveliness.

The fabric crease recovery was measured in the warp direction (with the crease in the filling direction) with the Monsanto Wrinkle Recovery Tester [1]. During this test, a sharp crease is imparted to the specimen, 1.5 cm wide, as it is folded and placed under a 1½ pound weight. After 5 min the weight is removed and the fabric permitted to recover from the crease. The angle formed by the two halves of the creased fabric after it has been allowed to recover for 5 min is considered a criterion of the fabric's tendency to show creases during wear, and is called crease recovery in this paper.

Results and Discussion

Fiber Properties

Stress-strain data are often used in experimental work for the evaluation of the merits of a new fiber type. They constitute a considerable saving over the evaluation of fabrics made from experimental fibers, and are generally considered to allow predictions of fabric properties accurately enough for screening purposes. But because even the production of fiber

[2] Vicara is the trade name of a regenerated zein fiber produced by the Virginia-Carolina Chemical Corporation, Taftville, Connecticut.

[3] These experiments were performed several years ago, and Vicara has since undergone some modifications of physical properties.

[4] This could perhaps be more precisely designated as "length recovery"; however, the terminology established by previous authors, e.g., [2], has been used in this paper.

TABLE I. Fiber Properties and Fabric Crease Recovery at Various Moisture Conditions

	Extension (%)	Relative Humidity 10%	65%	95%	Wet	10%	65%	95%	Wet	10%	65%	95%	Wet
		Vicara				Wool				Viscose Rayon			
Work recovery (%)	4	36	56	26	21	49	76	51	55	35	31	52	55
	6	28	37	21	19	33	55	46	52	—	26	47	49
	10	19*	23	20	20	—	31	41	48	—	22	35	37
	20	—	15	—	23*	—	19	39	47	—	—	20	—
Tensile recovery (%)	4	67	77	51	44	74	94	90	91	62	57	78	70
	6	54	64	44	41	61	80	87	94	—	47	72	69
	10	37*	48	37	38	—	59	85	95	—	38	63	59
	20	—	33	—	41*	—	42	87	96	—	—	47	—
Load (g/den)	4	0.90	0.53	0.26	0.16	1.08	0.54	0.28	0.21	2.10	0.77	0.23	0.22
	6	0.97	0.55	0.30	0.18	1.27	0.69	0.31	0.24	—	0.95	0.34	0.32
	10	1.21*	0.57	0.36	0.23	—	0.74	0.35	0.28	—	1.28	0.50	0.42
	20	—	0.70	—	0.36*	—	0.84	0.41	0.47	—	—	0.74	—
	Break	1.08	0.82	0.54	0.43	1.28	1.25	0.84	0.85	2.57	1.38	0.78	0.61
Elongation at break (%)		8.4	26.6	16.3	20.0	9.4	41.4	39.7	33.3	5.6	12.8	22.8	18.0
Compliance ratio (den/g)		0.64*	1.66	1.99	3.09	—	1.02	2.38	2.79	—	0.43	0.42	0.94
Young's modulus (g/den/%)		0.46	0.20	0.20	0.12	0.50	0.21	0.13	0.10	1.03	0.39	0.05	0.04
Work to stretch 4% ($ergs/cm^3 \times 10^8$)		0.31	0.14	0.10	0.06	0.32	0.10	0.08	0.07	0.59	0.22	0.05	0.04
Work recovered from 4% stretch ($ergs/cm^3 \times 10^8$)		0.11	0.08	0.03	0.01	0.15	0.07	0.04	0.04	0.21	0.07	0.03	0.02
Fabric crease recovery (%)		72† 65‡	80† 70‡	59† 27‡	32† 18‡	62	83	43	15	73	53	38	34

Note: A dash signifies that the majority of the fibers broke before this extension was reached.

* Several of the fibers broke before this extension was reached; the value given represents the average of the fibers which did not break.

† Suiting fabric.

‡ Filter fabric.

load-elongation curves and the measurements on them are tedious and time consuming, it was of interest to establish: (1) the minimum number of parameters needed to characterize a fiber type, and (2) the effect of relative humidity on these properties. The latter was studied because of the desire to predict with reasonable accuracy the behavior of the fibers at any humidity from measurements at standard conditions.

The data of Table I and Figure 1 show that, for the three fibers used in this work, there exists a rather close relationship between tensile and work recovery at humidities varying from 10% to the wet state, and at extensions varying from 4 to 20%. Beste and Hoffman [2] obtained similar results. In the present measurements, the high recovery values deviated more widely from a linear relationship than the lower values, i.e., those below about 40% work recovery or 70% tensile recovery. The practical result of this finding is that, to a first approximation, it is not too important which recovery, work or tensile, is calculated. Work recovery is easier to obtain where an automatic integrator is used to express the area under the load and relaxation curves, tensile recovery where such a device is not available.

Figures 2, 3, and 4 show the relationships between extension and work recovery obtained at 10, 65 and 95% relative humidity and in the wet state. It can be seen that the work recovery of wool decreases sharply as the extension is increased at low humidities, but the curve flattens out for 95% relative humidity and the wet state. Had the tensile recovery been plotted against extension, this flattening out of the curves representing results obtained at high relative humidity would be even more pronounced.

Vicara (Figure 3) shows very similar behavior with respect to work recovery except that the recovery values are generally on a somewhat lower level. The tensile recovery of Vicara decreased with in-

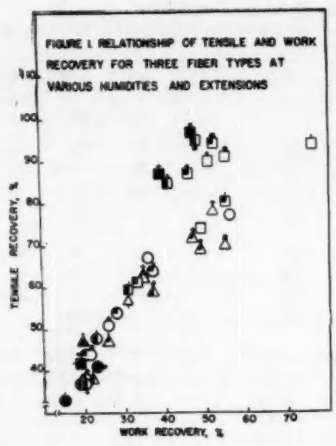
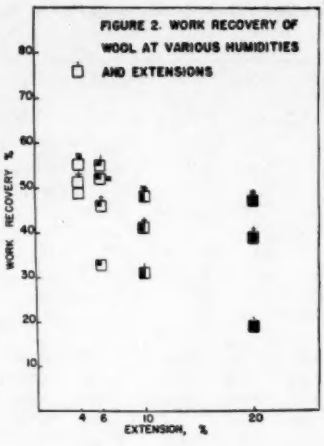
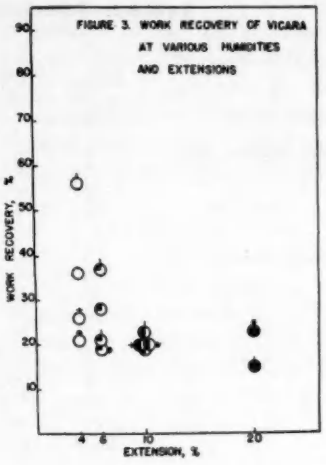
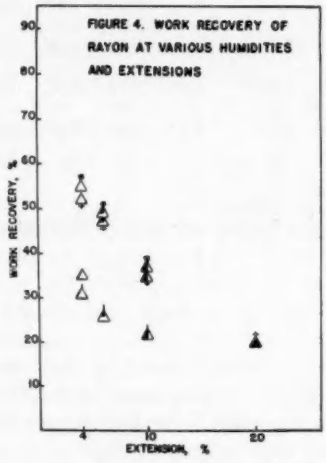


FIGURE 1. RELATIONSHIP OF TENSILE AND WORK RECOVERY FOR THREE FIBER TYPES AT VARIOUS HUMIDITIES AND EXTENSIONS
TENSILE RECOVERY, %
WORK RECOVERY, %







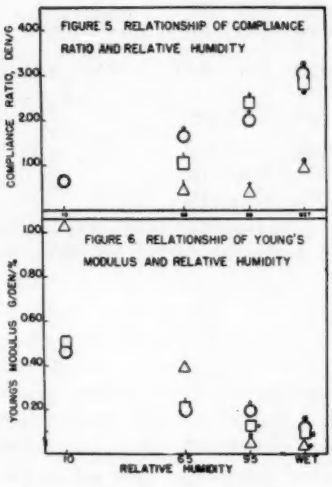
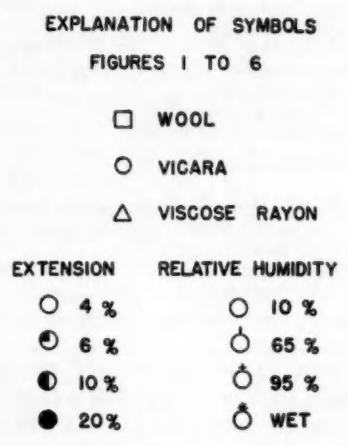


FIGURE 5. RELATIONSHIP OF COMPLIANCE RATIO AND RELATIVE HUMIDITY
COMPLIANCE RATIO, DEN/G
FIGURE 6. RELATIONSHIP OF YOUNG'S MODULUS AND RELATIVE HUMIDITY
YOUNG'S MODULUS G/DEN/%
RELATIVE HUMIDITY
WET

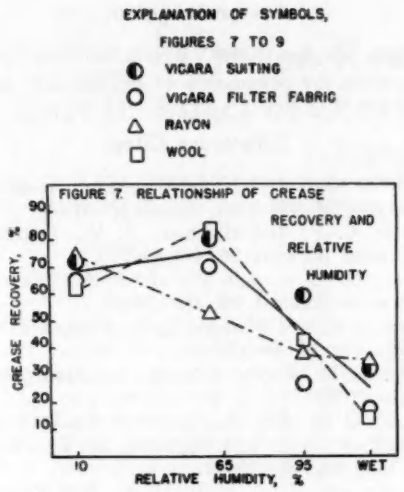


creasing extension at 95% relative humidity and was essentially independent of extension when wet. Viscose rayon (Figure 4) decreased in work and tensile recovery with increasing extension at all humidities. However, the trend shown by Beste and Hoffman's [2] paper is similar to that of the present data, especially for wool and the regenerated protein fiber.

The actual values of work to stretch the fibers to 4% extension and of the work recovered from the fibers were permitted to contract from this extension are shown in Table I. Here again the similarity of the behavior of the two protein fibers, wool and Vicara, is noteworthy. Rayon requires more work to stretch and returns more work when dry, and less when wet, than wool. The absolute values of work to stretch and work recovered, rather than their ratio (the work recovery) may be important in theoretical considerations of certain aspects of spinning of blends and in the engineering of industrial textiles. A minimum value of work returned by a fiber upon unloading may also be important for satisfactory crease recovery.

The effect of relative humidity on the compliance ratio (Figure 5), a property derived as described above from the load at two extensions, shows that rayon has a low compliance ratio at all humidities, while the compliance ratio of both protein fibers is higher and increases steadily with increasing humidity.

The Young's moduli of the fibers, as expressed by the slope of the linear (initial) portion of the stress-strain curve at various humidities, are shown in



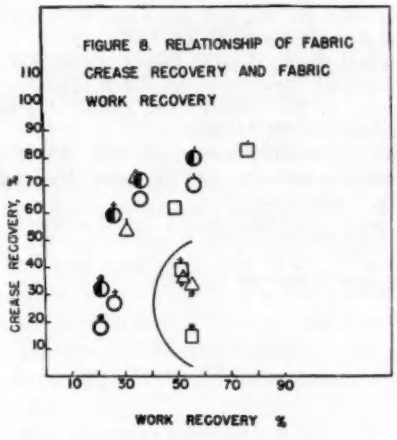


Figure 6. Rayon's modulus is higher when dry and lower when moist than the moduli of the two protein fibers, which are similar with respect to this property. Experience has shown that fibers which are similar in compliance ratio and Young's modulus result in fabrics of similar "hand."

Relationship between Fiber and Fabric Properties

Figure 7 shows the effect of humidity on the crease recovery of fabrics. The rayon fabric decreased steadily in crease recovery with increasing humidity; the maximum crease recovery of the protein fiber fabrics was reached at 65% relative humidity. It will be remembered that the maximum recovery values of the fibers are also reached at that humidity.

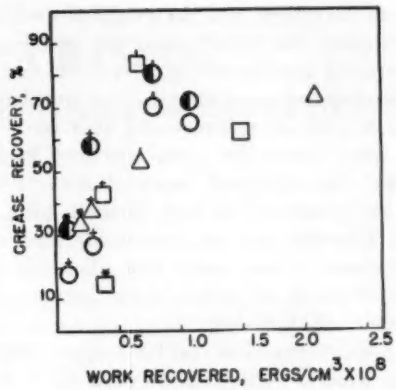


FIGURE 9. RELATIONSHIP OF FABRIC CREASE RECOVERY AND WORK RECOVERED BY THE FIBERS UPON RETRACTION FROM 4% EXTENSION

Theoretical considerations indicate that, in the creasing of a fabric, fiber extensions of not more than 10% occur and that the average extension may well be much lower. Present experience as well as that of others [2] has shown that the best correlation of fiber recovery properties with fabric crease recovery exists at extensions of about 5%. The relationship of crease recovery and fiber work recovery from 4% extension is shown graphically in Figure 8. Similar graphs are obtained if work recovery from 6% extension or tensile recovery from 4 or 6% are chosen as abscissa. For relative humidities of 10 and 65% a fair correlation exists between these properties, but at higher moistures is is obviously poor, especially for wool and rayon. Figure 9 illustrates the relationship obtained when the crease recovery is plotted against the absolute values of the work recovered after 4% extension. This relationship, too, is at best of a general nature, although one could assume the magnitude of the energy which is available to uncrease the fabrics to be important. Many factors influence the fabric crease recovery results and mask any direct dependency on fiber properties. Of these variables, the fabric construction will be treated in Part II of this paper. Other factors influencing these specific data may be differences in internal friction of the fabrics at various humidities, and certain shortcomings of the crease recovery test for moist and wet fabrics. Thus, the fabrics tend to

adhere to the clamps, and the weight of the absorbed water impedes the straightening out of the creased fabric against gravity and so affects the test result. It is therefore not surprising that the correlation between fabric crease recovery and fiber recovery becomes worse when the actual recovery forces are small and the additional factor of water retention enters the picture. The two Vicara fabrics, which differed in weight and construction, differed more in crease recovery when moist than when dry though the properties of the fibers taken from them were not significantly different.

The present data show that there apparently exists a rather general correlation between fiber recovery and fabric crease recovery, especially when measured at normal and low humidities. However, the possibility of other fiber properties correlating better with crease recovery should not be discounted. Similar work performed in this laboratory on resin-treated filament viscose rayon fabrics, both at 65% relative humidity and wet, showed that the sum of work expended to stretch the fibers 4% of their length plus the work recovered upon relaxation correlated better with the crease recovery than any other fiber parameter. There is still ample room for experimental work and thought along these lines, and the question of which fiber parameter or which combination of parameters have the greatest effect on fabric crease recovery remains unanswered.

Acknowledgment

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Crease Recovery of Fabrics

Part II: Effect of Construction on Crease Recovery of Fortisan Fabrics[1]

J. F. Krasny,[2] G. D. Mallory,[3] J. K. Phillips,[3] and A. M. Sookne[2]

Abstract

An attempt has been made to establish some general relationships between crease recovery and variables of fabric construction by an investigation of 174 systematically varied Fortisan filament fabrics. Crease recovery is generally improved by open construction, i.e., for any one fabric weight, by employment of high yarn denier and wide yarn spacing, and of open weave, i.e., one with long floats. In the case of asymmetrical weaves (e.g., 2/1 or 5/1 twills) the crease recovery is higher when measured with the longer float outside the crease. In general, little effect on crease recovery was found if the yarn properties were varied only in the filling direction.

Introduction

Part I of this paper represented an attempt to correlate certain fiber stress-strain properties with fabric crease recovery. The present paper describes the range of crease recovery values obtained in a series of fabrics made from one fiber, ¾ denier filamentous Fortisan. This basic material was made up into 174 fabrics differing widely in yarn denier and twist, weave, and ends and picks per inch. The fabrics were designed primarily for evaluation for industrial use; the series represented, however, an opportunity to study the effect of fabric construction on various textile properties, of which the crease recovery is discussed here.

The textile literature contains relatively few references to the relationship between fabric construction and crease recovery. Jameson et al. [4], who worked with a series of 32 plain-weave viscose rayon filament fabrics, found no significant effect of filling denier and picks per inch on crease recovery, although their fabrics varied systematically with these parameters in the other properties investigated. Hamburger et al. [3], working with acetate filament and staple fabrics, found some effect of weave on crease recovery; the effect of texture was more pronounced in staple yarn than in filament fabrics, while the effect of twist was not large. The same paper also contains a thorough theoretical analysis of the strains in the fabrics during creasing in conjunction with their construction. Buck and McCord's survey [2] contains some general statements about the relationship of fabric and yarn characteristics and crease recovery. However, there is a dearth of specific information on this subject, and it was therefore of interest to obtain additional data in this important field.

Materials and Methods

The basic material for all the fabrics were Fortisan filaments, nominally ¾ denier, with the following properties at 70°F and 65% relative humidity when tested at a rate of extension of 10% per minute:

Breaking load	5.5 g/den
Elongation at break	5.4%
Work to break	1.68×10^8 ergs/cm³
Young's modulus	1.73 g/den/%
Work to stretch, 4% extension	1.31×10^8 ergs/cm³
Work recovered, 4% extension	0.60×10^8 ergs/cm³
Work recovery from 4% extension	46%
Tensile recovery from 4% extension	56%

The fibers tested were taken from the warp of a desized fabric.

The fabrics can be divided into three groups:

1. *Balanced series,* containing the same number of yarns per inch and yarn type in both warp and filling.
2. *Unbalanced series,* i.e., two series of fabrics, each with constant warp but varying in filling denier and picks per inch.

[1] Contribution No. 214 from the Goodyear Tire and Rubber Company, Research Laboratory.

[2] Harris Research Laboratories, Inc., Washington, D. C.
[3] Goodyear Tire and Rubber Company, Akron, Ohio.

TABLE I. Effect of Denier, Texture, and Weave on Crease Recovery: Balanced Fabrics

Yarn		Ends and Picks per Inch	Weight (oz/ sq yd)	Cover Factor†	Position of Longer‡ Float	Crease Recovery (%)																			
						Plain Weave		Basket Weave				Twill Weave												Sateen Weave			
								2×2		12×12§		2/1		5/1		11/1		2/2		4/2		10/2		4/4		4 shaft		8 shaft	
Denier	Ply*					W	F	W	F	W	F	W	F	W	F	W	F	W	F	W	F	W	F	W	F	W	F	W	F
30	2	116	1.8	12.4	0	48	53	68	70	66	70	54	60	78	77	75	82	69	71	67	74	78	75	74	67	73	72	69	76
					I							68	72	63	67	66	72			71	65	79	72			72	68	74	61
30	2	167	2.6	17.7	0	—	—	60	61	61	60	52	50	75	77	77	78	57	62	70	69	71	78	71	66	69	66	74	77
					I							33	47	56	60	57	58			57	61	69	66			54	61	63	73
90	1	80	1.9	10.4	0	62	64	74	76	75	74	74	63	81	77	77	77	70	71	71	75	81	80	77	76	67	73	80	80
					I							69	67	77	77	76	75			75	71	80	74			70	78	76	73
90	1	118	2.8	15.3	0	—	—	60	64	61	67	48	56	73	72	78	78	61	63	71	72	78	75	67	70	64	72	73	60
					I							43	59	48	61	58	64			60	67	69	69			60	66	68	73
60	2	60	1.8	8.9	0	64	62	72	76	—	—	73	73	78	69	—	—	78	74	70	73	—	—	78	82	76	73	—	—
					I							70	73	69	77	—	—			78	74	—	—			75	75	—	—
60	2	90	2.9	13.4	0	—	—	70	66	65	71	59	66	65	76	70	82	63	67	66	75	67	80	66	74	61	73	72	78
					I							61	64	62	57	58	72			61	65	53	70			67	71	65	78
60	3	40	1.8	7.4	0	—	—	77	—	—	—	82	—	—	—	—	—	—	—	—	—	—	—	73	78	—	—	—	—
					I							81	—	—	—	—	—			—	—	—	—			—	—	—	—
60	3	60	2.8	11.1	0	62	65	75	74	72	77	65	68	75	77	77	74	69	72	75	77	69	81	76	76	69	73	80	79
					I							67	66	66	73	65	69			75	74	79	79			68	77	75	77
90	2	40	1.9	7.4	0	—	—	82	83	—	—	75	85	—	—	—	—	78	68	—	—	—	—	77	74	81	81	—	—
					I							79	81	—	—	—	—			—	—	—	—			79	81	—	—
90	2	60	2.9	11.1	0	—	—	—	—	—	—	68	68	78	77	—	—	67	70	80	76	—	—	69	79	76	80	—	—
					I							69	71	70	76	—	—			78	78	—	—			70	76	—	—
90	4	32	2.9	8.2	0	75	74	75	76	—	—	77	76	76	82	—	—	72	77	74	75	—	—	83	80	76	75	—	—
					I							75	72	78	82					75	79	—	—			79	77	—	—

* Single twist 2.5 S; ply twist: $36.5\sqrt{\text{denier}}$ Z.

† Cover factor = 0.0137 × yarns per inch × $\sqrt{\text{denier}}$; in balanced fabrics, the same in warp and filling.

‡ 0 means longer float on outside of crease; I means longer float on inside of crease.

§ 12 × 12 basket weave had a twill line.

TABLE II. Effect of Denier and Texture on Crease Recovery: Unbalanced Series (2×2 Basket Weave)

Filling Yarn		Picks per Inch	Filling Cover Factor	Crease Recovery	
Denier	Ply*			Warp (%)	Filling (%)
A. *Warp* 30/2, 116 *Ends per Inch, Cover Factor* 12.4					
60	1	126	13.4	65	70
30	2	116†	12.3	68	70
60	2	62	9.2	71	71
60	2	90	13.4	61	71
60	3	42	7.7	71	73
60	3	60	11.0	74	74
60	3	92	16.9	66	67
90	4	59	15.4	71	69
B. *Warp* 60/3, 60 *Ends per Inch, Cover Factor* 11.1					
60	1	51	5.4	74	72
60	1	87	9.2	65	70
60	2	60	9.0	73	71
60	2	88	13.1	74	57
60	3	41	7.5	80	79
60	3	60†	11.0	75	74
90	4	31	8.1	79	68
90	4	60	15.6	69	76

* Single twist: 2.5 S turns per inch; ply twist: $36.5\sqrt{\text{denier}}$ Z.
† Balanced fabric.

3. *Twist series,* in which the filling denier, number of plies, and twist were varied.

1. *Balanced Series*

The specifications of the balanced series are given in Table I. These fabrics were produced in two groups, weighing approximately 2 and 3 oz/sq yd, respectively. The yarns used had the following denier/ply combinations: 30/2, 60/2, 60/3, 90/1, 90/2, and 90/4; the number of yarns per inch varied from 30 to 166. The cover factors [4] varied from 7.4 to 17.7, a much wider range than would be practical for apparel fabrics. Each series, i.e., each group incorporating one type of yarn in either 2- or 3-oz construction, was woven in eleven or twelve weaves. (The plain weave could not be woven in the case of the tightest textures.) The producer's single twist of all yarns was 2.5 S turns per inch; the ply twist factor was 0.5, the ply direction Z. The 90/1 yarn also had this twist factor.

2. *Unbalanced Series*

Table II gives the specifications of the two unbalanced series, i.e., fabrics woven from two warps with filling varying from 60/1 to 90/4. These fabrics

[4] The cover factor is a measure of tightness of weave. For rayon fabrics, it is defined by the relationship: cover factor = 0.0137 × yarns per inch × $\sqrt{\text{denier}}$.

TABLE III. Effect of Filling Twist and Number of Plies on Crease Recovery *

2/2 Twill						2×2 Basket					
Filling Twist				Crease Recovery		Filling Twist				Crease Recovery	
Single (t.p.i.)	Ply (t.p.i.)	Resultant Single Twist (t.p.i.)	Picks per Inch	Warp (%)	Filling (%)	Single (t.p.i.)	Ply (t.p.i.)	Resultant Single Twist (t.p.i.)	Picks per Inch	Warp (%)	Filling (%)
Filling: 60/1											
2.2 S	—	2.2	155	70	56	2.0 S	—	2.0	155	66	56
9.1 S	—	9.1	148	69	49	10.5 S	—	10.5	148	66	65
21.9 S	—	21.9	148	60	51	—	—	—	—	—	—
Filling: 60/2											
2.3 S	10.1 S	12.4	86	62	63	2.3 S	10.0 S	12.3	88	64	57
2.6 S	15.0 S	17.6	84	66	62	2.6 S	14.9 S	17.5	86	61	60
2.5 S	18.1 S	20.6	85	65	60	2.5 S	13.0 S	15.5	85	63	71
10.4 S	10.7 S	21.1	85	63	61	10.4 S	10.1 S	20.5	86	63	62
13.4 S	9.7 Z	3.7	87	67	64	13.4 S	9.6 Z	3.8	87	71	63
10.4 S	17.6 Z	7.2	85	68	65	10.4 S	17.2 Z	6.8	88	70	66
22.3 S	10.0 S	32.3	85	65	64	22.3 S	10.0 S	32.3	85	65	77
21.0 S	9.4 Z	11.6	86	66	57	21.0 S	4.0 Z	17.0	85	73	72
Filling: 60/8											
2.4 S	9.9 S	12.3	43	64	76	2.4 S	9.4 S	11.8	44	62	79
10.9 S	10.6 S	21.5	43	59	79	10.9 S	10.6 S	21.5	42	66	77
10.3 S	9.3 Z	1.0	43	62	68	10.3 S	10.8 Z	0.5	42	76	72
23.3 S	23.4 Z	0.1	42	73	52	23.3 S	23.3 Z	0.0	42	85	49

* Warp: 60/2, 2.5 S single twist, 3.2 Z ply twist, 97 ends per inch.

were woven only in 2 × 2 basket weave, and their yarn twist was the same as that used in the balanced series.

3. *Twist Series*

Table III shows the various filling deniers and numbers of plies and picks per inch which were used in conjunction with one 60/2 warp. These fabrics were woven in both 2/2 twill and 2 × 2 basket weaves.

All measurements were performed on desized samples. The crease recovery tests were made with the Monsanto Wrinkle Recovery Tester [1] at 65% relative humidity and 70°F. Some of the fabrics available could not be tested because of their open construction. Crease recovery measurements were made even on those fabrics which were too sleazy for apparel use, to facilitate analysis of the data.

Results and Discussion

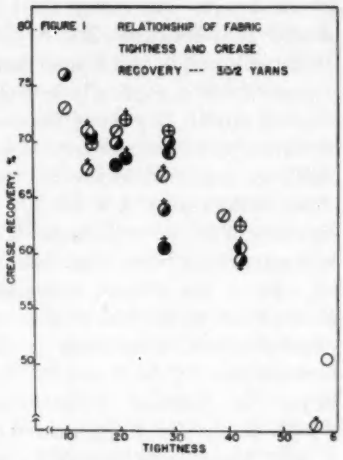
Part I of this paper contains a discussion of the general correlation between certain fiber properties and fabric crease recovery. If the value for work recovery of Fortisan from 4% extension—46%—is plotted on Figure 8 of Part I, a crease recovery of approximately 70% is implied; the same result is obtained when the work recovered by the fiber after 4% extension is plotted in Figure 9. From Tables I to III of Part II of this paper it can be seen that this corresponds roughly to the modal value of crease recovery of the numerous fabrics involved. But more significant than this interpolation in the widely dispersed correlation graphs may be the finding that the crease recovery ranges from 33 to 85% in these fabrics, all of which were lightweight, produced from the same fiber in a filament form, and not finished in any manner. The frequency distribution of crease recovery values is skewed to the left, i.e., only about 2% of all values are below 50, 5% between 50 and 60, 31% between 60 and 70, 54% between 70 and 80, and 8% above 80% crease recovery. This compilation should not lead to the conclusion that Fortisan fabrics usually have crease recoveries in these ranges; as a matter of fact, the fabrics with constructions dense enough for use in apparel have crease recovery values in the lower classes enumerated here. The object here is primarily to show the magnitude of the spread in this property obtainable solely by variation of certain fabric parameters, with fiber properties constant.

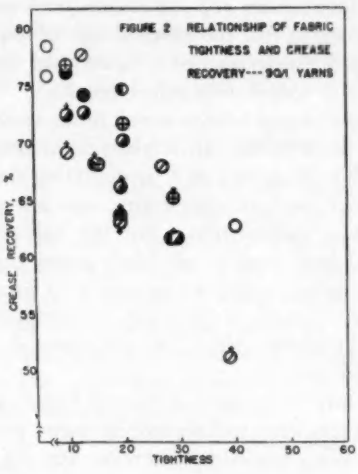
Hamburger et al. [3] have analyzed in great detail the fiber strains during creasing as a function of yarn diameter and cross-sectional shape and of texture and weave. The strains and thus permanent extensions of the fibers are increased by short floats, high cover factors, and yarns which do not tend to flatten in the fabric. In addition, more opposition due to internal fabric friction is met by the recovery forces of the strained fibers in a tight fabric (high cover factor, short floats), and these forces are thus less efficiently used in uncreasing tight than open fabrics. As a measure of fabric tightness, the number of weave repeats per inch was arbitrarily chosen for the abscissas of Figures 1 to 5. This is the number of yarns per inch divided by the number of yarns per weave repeat, i.e., the number of yarns of any system, warp or filling, at which a weave repeats itself.[5] Since any one yarn appears on the face fabric side as well as on the back in each repeat, and crosses again to the face side at the end of the repeat, the tightness numbers are also one-half the number of interlacings of the yarns per inch. A high tightness number thus represents a high number of yarns per inch combined with a low number of yarns per weave repeat, i.e., a short-float weave. This number thus does not take the denier into account; however, each of Figures 1 to 5 represents fabrics woven with one yarn denier in various weaves and, in Figures 1 to 3, two weights or textures. Each point in Figures 1 to 6 represents the average crease recovery of warp and filling; these are considered separately in Figures 7*A* and *B*.

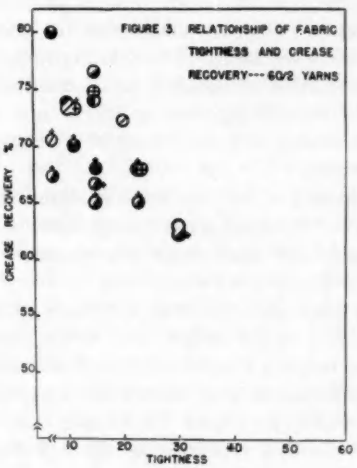
The most important fabric construction factor affecting the crease recovery of the balanced fabrics was found to be the tightness. Figures 1 to 5 represent the crease recovery-tightness relationship, each for a different yarn denier and ply combination. They are all quite similar, which indicates that, in fabrics of similar weight, the yarn construction has less effect on crease recovery than the combined effect of yarns per inch and weave. In other words, it seemed to make little difference whether, e.g., the 3-oz fabrics were woven with 30/2 yarns, 107 to the inch, or 60/3 yarns, 60 to the inch, if the number of weave repeats per inch was kept constant.

An attempt can now be made to analyze the separate effects of tightness, texture, and weave. For any one position on the tightness scale and any one yarn type, the crease recovery of the 3-oz fabrics (tighter texture, longer floats) tends to be lower

[5] The number of yarns per weave repeat is two for the plain weave, three for the 2/1 twill, four for the 2/2 twill, 2 × 2 basket, and 4-shaft sateen, six for the 4/2 and 5/1 twills and the 12 × 12 basket with twill line, eight for the 4/4 twill and 8-shaft sateen, and twelve for the 10/2 and 11/1 twills.







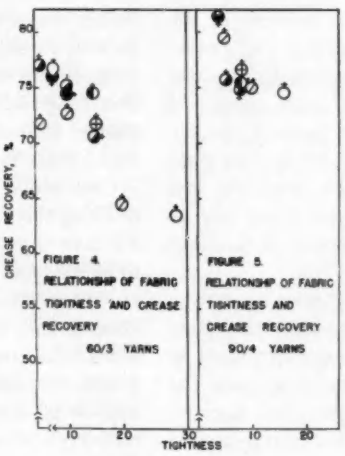


FIGURE 4. RELATIONSHIP OF FABRIC TIGHTNESS AND CREASE RECOVERY 60/3 YARNS
FIGURE 5. RELATIONSHIP OF FABRIC TIGHTNESS AND CREASE RECOVERY 90/4 YARNS
CREASE RECOVERY, %
TIGHTNESS

EXPLANATION OF SYMBOLS FIGURES 1 TO 5

- ○ PLAIN
- ⊘ 2/1, 5/1, 11/1, TWILL
- ◑ 2/2, 4/2, 10/2, TWILL
- ◒ 4/4 TWILL
- ◐ 2/2 BASKET
- ● 12/12 BASKET
- ⊕ 4, 8, SHAFT SATEEN
- \+ 3 OUNCE FABRIC

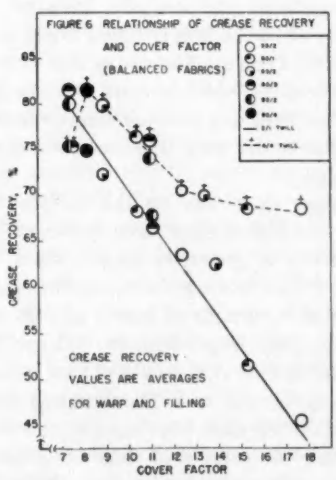
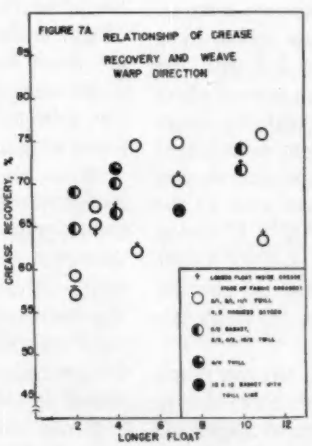
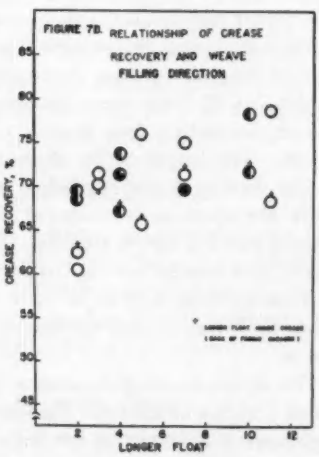


FIGURE 6. RELATIONSHIP OF CREASE RECOVERY AND COVER FACTOR (BALANCED FABRICS)
CREASE RECOVERY VALUES ARE AVERAGES FOR WARP AND FILLING
CREASE RECOVERY, %
COVER FACTOR





than that of the 2-oz fabrics (opener texture, shorter floats). Thus it seems that the effect of tighter texture, which reduces crease recovery, outweighed the beneficial effect of a weave with longer floats.

The crease recoveries of fabrics woven in the same weave with the same yarns but differing in weight can be compared in Figures 1 to 3 by observing the relative position of symbols representing one weave in the 2- and 3-oz construction. For the tightest weave which had been used for all fabric series, the 2/1 twill, the increase in texture necessary to produce a 3-oz rather than a 2-oz fabric lowered the crease recovery by about 15%. This difference decreased for opener weaves.

Similarly, for any one weave, the cover factor, a function of yarn diameter and number of yarns per inch, was fairly closely related to the crease recovery. This is shown for the tight 2/1 twill and the open 4/4 twill in Figure 6. The crease recovery of the 2/1 twills differing in yarn construction and denier as well as in texture decreased essentially linearly with increasing cover factor. The more open 4/4 twills behaved in somewhat similar fashion, but the rate of decrease is generally lower, and may be quite small at higher cover factors. The relatively low values for the 4/4 twill at the lowest cover factors can perhaps be explained by the difficulty of handling these very sleazy fabrics during the test.

Figures 7*A* and *B* represent an attempt to analyze the effect of weave separately and to show the effect of the manner in which the floats are distributed in a weave repeat. Here each point represents the average crease recovery of all fabrics with a cover factor above 10 (except that of the fabrics woven with sixty 90/2 yarns per inch) in the weave indicated. As abscissa, the length of the longer float (the larger number of yarns of one system, warp or filling, which are crossed over in any weave by a yarn of the other system, e.g., two for 2/1 twill, ten for 10/2 twill) was chosen as allowing a more effective representation than number of yarns per weave repeat. The length of the shorter float is indicated by the shading of the symbols. Longer and shorter floats are equal in symmetrical weaves such as the baskets and 2/2 and 4/4 twills. The 12 × 12 basket weave was woven with a twill line, and its longer float varied from 4 to 10 in each repeat; an abscissa value of 7 was chosen arbitrarily to represent this weave.

The variations in crease recovery in any one fabric series (fabrics of identical yarn and texture) due to weave are of a somewhat smaller order of magnitude than those caused by tightness variations for fabrics of one weave. Increasing the longer float with the shorter float constant (2/1, 5/1, 11/1 and 2/2, 4/2, 10/2 twills and 4- and 8-shaft sateens) increased the crease recovery, especially between the shortest and medium floats. Increasing the shorter float increased the average crease recovery in the case of the 2/2 twills as compared to the 2/1 twills, but had little effect in the case of 4/4 and 4/2 twills. The crease recovery of the 12 × 12 basket fabrics with twill line was usually not better than that of the 2 × 2 baskets in spite of the sleazier appearance of the fabrics, perhaps due to internal strains caused by this complicated weave. There was no significant difference between the 2/2 twill and the 2 × 2 basket fabrics in both the balanced (Table I) and the twist series (Table III). The 4-shaft sateen could be considered a tight weave with respect to its effect on crease recovery, while the 8-shaft sateen showed perhaps higher crease recovery than its position on the float scale or its sleaziness warrants. The data imply that perhaps the combination of sateen type of distribution of points of interlacing over a fabric and a shorter float of 2 instead of 1 may result in relatively high crease recovery.

One more parameter had to be considered in drawing the graphs: the fabrics were warp-flush, i.e., the side with the longer warp floats was considered to be the face. In Figure 7*A* (warp crease recovery) an unmarked symbol indicates that the fabric was creased with the face or the longer float on the outside of the crease, while a symbol marked + denotes a measurement with the back or shorter floats on the outside of the crease. In Figure 7*B* (filling crease recovery) those symbols representing short filling floats on the outside are again marked with +, while the unmarked symbols represent the back of the fabric, or the case when the longer filling floats were on the outside of the crease. The distinction may be important for fabrics in which creases are inserted directionally rather than in a random manner in use, e.g., at right angles to the warp in sleeves and at the knees of pants legs.

When the longer float was on the outside, the crease recovery was higher than when it was on the inside; this effect was generally larger when the shorter float was 1 than when it was 2, and increased as the difference in the length of longer and shorter float increased, e.g., was larger than the 5/1 or 10/2 twill than for the 2/1 or 4/2 twill. These results are generally in agreement with Hamburger's theoretical considerations of yarn buckling [3].

If one considers the individual data of Table I, several interaction effects can be detected. Thus the

differences between the crease recovery measured with the longer float outside and inside the crease, respectively, are larger when the texture is dense, and lower when it is more open. Similarly, the lowering of crease recovery due to short floats is less severe in the fabrics with more open texture. Furthermore, the warp crease recovery is generally slightly lower than the filling crease recovery, perhaps indicating an effect on the elastic behavior of the warp yarns of the more severe strains they undergo in weaving.

As could be expected, the variations in crease recovery when only the texture and yarn construction of the filling was varied, as in the two unbalanced series (Table II), were relatively small. This may be partially due to the fact that the weave chosen, 2×2 basket, is relatively open and less sensitive to texture changes than, e.g., 2/1 twills. On the other hand, Jameson [4], working with similar variations in the filling direction of plain weave rayon fabrics, found no significant correlation of the crease recovery with the varied parameters, and Hamburger [3] reports similar results for acetate filament fabrics. In the present two series, of the pairs of fabrics woven with one filling denier, increasing texture frequently reduced warp and/or filling crease recovery, while the increase in filling cover factor or denier could not be related to either crease recovery. The cover factors of the single, 2-ply and 8-ply filling fabrics of the twist series (Table III) varied only slightly, but the filling crease recovery increased quite considerably with increasing number of plies and thus denier, and concurrent decrease in filling texture. The warp crease recovery represented no clear picture.

The data of Table III show that changing the filling twist did not produce consistent, obvious changes in filling crease recovery. The warp crease recovery of the fabrics with single-ply filling seemed slightly higher than that of the fabrics with 2-ply filling. Reversals in the filling twist, i.e., Z ply twist and S singles twist, affected the warp crease recovery favorably, possibly slightly more so in the basket weave than the twill fabrics.

One unplanned variable entered this experiment. All fabrics of the balanced series had approximately equal amounts of warp and filling crimp except for one series. The series woven with ninety 60/2 yarns per in. had essentially no warp crimp and inordinately high filling crimp, presumably due to higher tension on the loom. This series did not conform to the general pattern of behavior in several properties, especially in thickness and air permeability, both of which were inordinately low. Its filling crease recovery exceeded the warp crease recovery by slightly more than average amounts; it is hard to say whether this was due to excessive warp strain or to an effect of crimp unbalance per se.

Conclusions

This work on the relationship of crease recovery and fabric construction parameters has been conducted using Fortisan, a strong fiber with relatively low extensibility, which is not widely used in apparel fabrics at present. Making the assumption that the data are nevertheless useful for guidance for the behavior of apparel fabrics, an assumption which seems justified in view of previously published data, the following can be stated.

In a filamentous fabric of a given weight, constructed from filaments of a given denier, the following measures should improve fabric crease recovery:

1. Reduction of fabric tightness by use (*a*) of the lowest number of yarns per inch and the highest denier consistent with the use of the fabric; and (*b*) of a weave with large longer floats and shorter floats of at least 2. This reduces fiber strain during creasing as well as internal friction, thus allowing the energy stored in the fiber (= recoverable work absorption) to uncrease the fabric with less interference.

2. Use of symmetrical weaves where crease formation is likely to be random, and weaves with one float longer than the other in such a manner that the longer float will be on the outside of and normal to creases usually forming in one direction.

3. Use of twist reversal in ply twisting, e.g., Z ply, S single twist, for improvement of the crease recovery in the system normal to that of the twisted one. For example, improvement of the warp crease recovery by the use of reversal in filling twist.

In general, however, changes of construction parameters in one direction only, warp or filling, have only slight effects on crease recovery.

Acknowledgment

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Interaction of Acid-Treated Wool and Silk with Water Vapor and Water[1]

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Abstract

Extensive results are given on the effects of HCl and picric acid on the capacity of wool to absorb water. Both the effect of changing the relative humidity and the effect of changing the acid content of the fibers were studied. Less extensive results were obtained using H_2SO_4, oxalic acid, and Orange II acid and salt on wool, and HCl on silk. Collateral measurements were also made on the swelling of human hair in picric acid solution and on the electrical resistance of wool fibers containing acid at various relative humidities.

The absorption of acid decreases the capacity of wool to absorb water at low and moderate relative humidities. The efficiency with which the absorption of water is reduced depends on the identity of the acid.

At the highest relative humidities the acids divide into two groups. In the case of the first group, of which picric acid is an example, the effect of acid on the absorption of water is the same as at lower humidities. In the case of the second group, of which HCl is an example, there is a second mechanism of interaction, which tends to increase the absorption of water and competes with the mechanism causing the decrease at lower relative humidities. The second mechanism may become dominant, causing a net increase. This has been shown by direct measurement and by analysis of swelling measurement.

The mechanism of interaction decreasing the absorption is identified as competitive absorption of acid on primary bonding sites for water. The mechanism of the interaction increasing absorption has been tentatively identified as osmotic absorption of water resulting from mobility of absorbed anions at the highest relative humidities. It is also possible that anion hydration is important in some cases.

THE PRIMARY purpose of the work described in this paper was the examination of the effect of absorbed acid on the capacity of wool and silk for absorbing water, and the interpretation of the results in terms of the mechanism of absorption of acid and water. Certain other measurements of the swelling of hair in acid solutions and of the electrical resistance of acid-treated wool fibers have also been included. The protein fiber-acid-water system is of importance in the textile field, and closely related systems are involved in biochemical and physiological processes. Although various protein-acid-water systems have been studied using liquid external phases, much less work has been done on absorption from the gas phase.

[1] This article is based in part on a dissertation to be submitted by Arthur F. Cacella in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. Presented before the Polymer Section at the 125th National Meeting of the American Chemical Society, March 29, 1954.

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At the start of this work some results on silk treated with HCl had been reported by Green [9], and some results on wool treated with H_2SO_4 by Das and Speakman [7].[4] As the work described in this paper was being written up, articles by Larose [17] and Nicholls and Speakman [20] on wool appeared. Finally, some as yet unpublished work by Hutton on silk was made available to the authors.[5] All these results will be discussed in some detail below.

Some measurements of collateral interest have also been reported. One of the acids used in the present experiments was HCl, which might be expected to be desorbed during the prolonged exposure to water vapor necessary for water-absorption measurements. The uptake of gaseous HCl was studied by Green [8, 9], using silk; Larose [16], using wool; and Benson and Seehof [5], using egg albumin. It was found in every case that a certain portion of the HCl was absorbed irreversibly. For silk and egg albumin, it was shown that the presence of water vapor or absorbed water did not promote the desorption of this portion of the HCl, although it can be removed by washing with liquid water. Since no HCl was lost during the experiments reported here, these results are confirmed for silk and shown to be true also for wool.

The interaction of protein fibers with aqueous acid solutions and the absorption of water by untreated proteins have been so widely studied as to need no further general discussion here. Specific references will be introduced where needed in the discussion.

Experimental

Preparation of the Samples

A medium-grade domestic wool which had been processed into a standard 13-oz square-weave fabric[6] was used. The fabric, which had received a commercial soap and soda scouring, was further purified by repeated washing with distilled water for 6 hr, continuous extraction in a Soxhlet apparatus with methyl alcohol and then with ethyl ether for 20 hr, followed by a final repeated washing daily for 4 days with distilled water of *p*H 5.8.

Samples of Italian spun silk broadcloth were similarly extracted and rinsed.

Preparation of Acids

Hydrochloric and sulfuric acids were diluted volumetrically to the concentrations required. Oxalic, picric, and Orange II acids were dried overnight in an oven at 60°C, weighed, and made up to the desired concentrations in distilled water.

The concentrations of picric and Orange II acids were checked by electrometric titration with sodium hydroxide, using a *p*H meter. The remaining acids were titrated with phenol red as indicator.

Acculute hydrochloric acid and reagent-grade sulfuric, oxalic, and picric acids were used without purification.

The sodium salt of Orange II (*p*-sulfobenzene-azo-β-naphthol) was purified by repeated salting out with sodium acetate, according to the method of Robinson and Mills [23]. The free acid was prepared by dissolving the salt in approximately 2 *N* hydrochloric acid and washing the precipitated dye acid with several portions of the same hydrochloric acid solution. The acid dye precipitate was air dried, then oven dried at 60°C, and finally dried over potassium hydroxide in a vacuum desiccator to remove the excess hydrochloric acid.

Treatment of Samples with Acids

In general, known dry weights of wool and silk between 1 and 2 g were immersed in 50- or 100-ml portions of acid of the desired concentration at a temperature of 20.5 ± 0.5°C for 72 hr. The individual samples were then removed from the acid solutions, drained with suction on a Buchner funnel, and immediately rinsed with 10 to 75 ml of distilled water from a pipet to remove excess acid solution. The samples were air dried and then dried in vacuo over magnesium perchlorate for 2 weeks, as described below, to obtain the dry weights of the acid-treated samples for water-absorption calculations.

Since the samples were rinsed, the acid uptake could not be determined by a change-of-titer method; and the acids were extracted from the fibers at the end of the water-absorption determinations.

The treatment of wool with Orange II differed from that used with the other acids in that the wool was held at a temperature of 60°C for 48 hr so that the maximum uptake at the given *p*H would be obtained. At lower temperatures equilibrium is reached

[4] After this paper was completed, similar work by Harris [*J. Research Natl. Bur. Standards* 12, 475 (1934)] was brought to the authors' attention.

[5] The authors wish to thank E. A. Hutton and S. G. Smith of the Shirley Institute, Didsbury, Manchester, for making their results available to them.

[6] This wool has been studied extensively in connection with the Wool Research Project of Textile Research Institute, under the code WC-3.

TABLE I. Solutions Used for Control of Relative Humidity

Solute	Relative Humidity (% at 20°C)	Reference
LiBr (saturated)	6.8	[19]
LiCl (saturated)	11.3*	[24, 31]
H_2SO_4 (58.3%)	20.0	[32]
$KC_2H_3O_2$ (saturated)	22.0*	[21, 31]
$MgCl_2$ (saturated)	33.5	[21]
K_2CO_3 (saturated)	44.0*	[21]
$Na_2Cr_2O_7$ (saturated)	54.0*	[6]
$NaNO_2$ (saturated)	66.0	[21]
NaCl (saturated)	75.7	[6]
KCl (saturated)	86.4	[21]
KNO_3 (saturated)	93.5	[21]
H_2SO_4 (10.0%)	96.0	[32]

* Checked by isopiestic measurements with H_2SO_4 as control.

too slowly for convenience. The rinsing and drying of the treated wool was carried out as discussed above.

Preparation of Constant-Humidity Solutions

Reagent-grade salts were used without purification to prepare the saturated salt solutions. Reagent-grade sulfuric acid, diluted to the appropriate concentration according to the data of Wilson [32], was used for some humidities. The solutions used and their relative humidities are given in Table I.

Potassium acetate, potassium carbonate, and sodium nitrite solutions might be expected to be unstable over a long period of time because of hydrolysis. These solutions were found to be stable over the period of 3 months during which the water-absorption measurements were made, as shown by the consistency of repeated water-absorption measurements on the same samples, and by several isopiestic measurements made using H_2SO_4 as a standard.

Water-Absorption Measurements

One- to two-gram samples of the untreated and acid-treated fabrics were placed in glass-stoppered weighing bottles, and dried for 2 weeks in vacuo (produced by a mechanical pump) over magnesium perchlorate in a desiccator at room temperature (about 25°C). At the end of the drying period, the vacuum was broken by admission of air dried by passage through two towers of magnesium perchlorate. The desiccator was then opened, and the bottles were immediately tightly stoppered to prevent reabsorption of moisture from the atmosphere. The bottles were equilibrated with the atmosphere and weighed. The "dry weight" thus obtained was found to be readily reproducible. Vacuum desiccators of 300-mm inside diameter containing 250 ml of humidifying solution in a crystallizing dish served as conditioning chambers. A watch glass separated the solution and the sample to minimize contamination from droplets. All conditioning was done at 20.5 ± 0.5°C.

All the water-absorption measurements were made on the adsorption cycle. The samples were dried, were placed over the proper salt solution, and the desiccator was evacuated. After a period of 2 weeks [7] the desiccator was filled with dry air and opened. The lids on the weighing bottles were immediately closed, and the samples were weighed.

In this way most of the samples were taken in steps of ascending humidity through all the humidities listed in Table I. After the final equilibration at 96% R.H., the samples were dried again over magnesium perchlorate to check the original dry weights.

All the determinations of amount of water absorbed were carried out at least in duplicate, and at least two separate determinations were made with each sample at every humidity, except the very highest. The coefficient of variation of the water-absorption values averaged about 2% at the two lowest humidities and about 1% at all other humidities.

For one set of measurements distilled water was used as the conditioning agent. Since it is very difficult to avoid condensation of water vapor on the fibers or bottles under such conditions, only those results were accepted for which there was no visible condensation of water on the surface of the fabrics or of the bottles.

Analysis of Acids in the Samples

The various acids were extracted from the samples at the conclusion of the water-absorption determinations. For hydrochloric, sulfuric, and oxalic acids the extraction was effected by means of 0.5% aqueous pyridine. The method was patterned after that of Barritt et al. [4] and consisted of immersing the treated wool and silk in 100-ml aliquots of 0.5% aqueous pyridine overnight. The extracted acid was

[7] Actually, it was found that many samples reached equilibrium in as little as 7 days, but the most consistent and reproducible results were obtained after 2 weeks.

TABLE II. Absorption of Water by Untreated and Acid-Treated Wool

Reagent	Reagent Content of Sample (mM/g)	Water Uptake $\frac{mM}{g\ dry\ wool}$ at Stated Relative Humidity: Relative Humidity (%) 6.8	11.3	20.0	22.0	33.5	44.0	54.0	66.0	75.7	86.4	93.5	96.0	[100]
Untreated	—	2.12	2.61	3.63	4.09	4.97	6.17	7.27	8.31	9.77	11.7	14.6	15.2	18.9
HCl	0.75	1.73	2.10	3.04	3.36	4.21	5.26	6.26	7.13	8.52	10.3	12.4	14.8	18.9
HCl	0.61	1.78	2.16	3.07	3.58	4.29	5.43	6.36	7.28	8.68	10.5	12.7	14.8	19.6
HCl	0.52	1.82	2.19	3.12	3.63	4.30	5.36	6.34	7.32	8.67	10.5	12.8	14.6	17.9
HCl	0.44	1.84	2.25	3.32	3.92	4.37	5.47	6.49	7.45	8.86	10.7	13.6	14.6	17.8
HCl	0.21	1.97	2.41	3.44	3.86	4.63	5.75	6.80	7.75	9.19	11.1	14.1	14.4	17.7
H_2SO_4	0.34	1.88	2.30	3.49	3.76	4.52	5.68	6.74	7.73	9.00	11.1	13.8	14.6	18.3
$(COOH)_2$	0.53	1.72	2.09	2.85	3.10	4.08	4.96	6.00	6.90	8.38	10.1	13.0	13.8	18.4
Orange II acid	1.08	1.74	2.15	3.24	3.65	4.32	5.36	6.26	7.22	8.37	10.2	12.7	12.7	15.2
Orange II salt	0.049	2.14	2.60	3.71	4.16	5.11	6.16	7.27	8.37	9.66	12.0	14.9	16.3	20.0
Picric acid	0.93	1.32	1.64	2.50	2.83	3.37	4.29	4.98	5.76	6.72	7.99	9.77	10.1	12.2
Picric acid	0.81	1.43	1.72	2.71	2.86	3.54	4.54	5.22	6.13	7.13	8.31	9.99	10.5	12.5
Picric acid	0.18	1.82	2.26	3.25	3.53	4.39	5.50	6.54	7.51	9.04	10.6	12.9	13.6	16.6
Picric acid	0.12	1.93	2.39	3.35	3.65	4.55	5.61	6.68	7.67	9.24	10.7	13.2	14.2	16.7

determined by titration with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator.

For the Orange II salt and acid, stripping of the dye from the fiber was accomplished with 25% aqueous pyridine and the concentration was determined spectrophotometrically.

Extraction of picric acid presented a more difficult problem, since the acid is held tenaciously by wool. It was found possible to extract it from the wool with 25% aqueous pyridine, but the procedure was time consuming; consequently, only one sample of each acid content was actually extracted and the acid determined. The values so found correlated well with change of titer values and with the acid contents derived from differences in dry weights of the wool before and after the original treatment with acid. Therefore, the amount of picric acid in each of the remaining samples was calculated on the basis of initial and final dry weights obtained before and after the acid treatment.

The acid contents listed in the tables are based on the amounts of acid extracted and are average values for two or more extractions for each acid content, except in the case of picric acid, as just mentioned.

Measurement of the Swelling of Human Hair in a Picric Acid Solution

Direct microscopic measurements were made at room temperature, using the equipment and method described by Barnard and White [3]. Measurements were made after 24, 48, and 72 hr.

Electrical-Resistance Measurements

Direct, single-fiber resistance measurements were made at 30°C, using the equipment and method of Hersh and Montgomery [13].

Results

Water-Absorption Measurements

Table II contains measurements of the amount of water absorbed by wool samples containing various amounts of acid, as a function of the relative humidity. The column labeled [100], referring to 100% R.H. was obtained using distilled water as the conditioning agent. Thus, in principle, the fibers were exposed to an atmosphere of 100% R.H. However, because of temperature fluctuations in the gas phase and resulting condensation and evaporation effects in the gas and on nearby surfaces, it is unlikely that an average relative humidity of more than 97% or 98% is maintained [1]. For this reason the humidity value is put in brackets to show its unreliability. Of course, if condensation occurs on the fiber sample, another source of error is present. As has been explained, an effort was made to avoid such an error. Figures 1 and 2 show various facets of the results in Table II.

In Table III and Figure 3, similar but less extensive results are shown for silk containing 0.12 mM/g of HCl.

In connection with the work on wool, it became desirable to know something about the water-absorb-

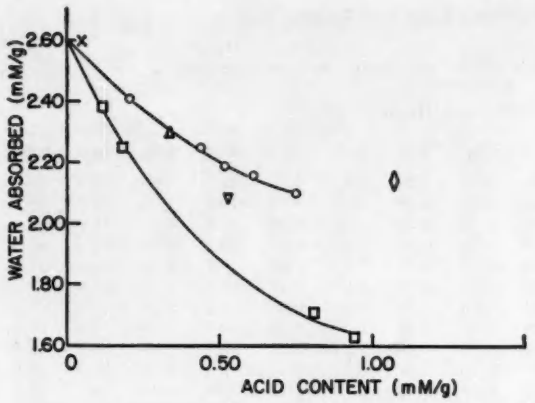

Fig. 1. Absorption of water by acid-treated wool at 11.3% R.H.: ○ HCl; □ picric acid; △ sulfuric acid; ▽ oxalic acid; ◇ Orange II acid; × Orange II salt.

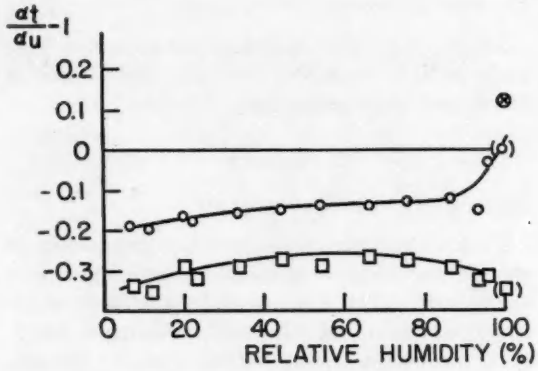

Fig. 2. Fractional increase in water absorbed by wool containing 0.75 mM/g HCl: ○ direct, ⊗ from swelling; and 0.81 mM/g picric acid: □ direct.

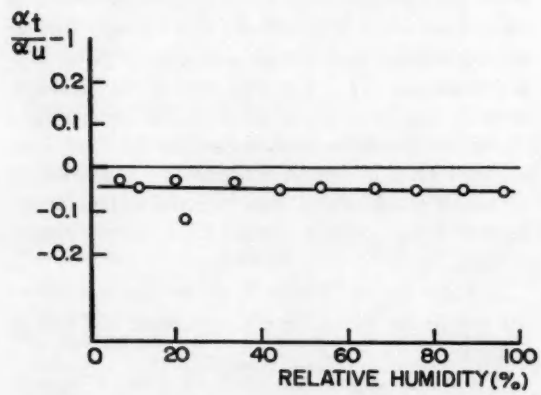

Fig. 3. Fractional increase in water absorbed by silk containing 0.12 mM/g HCl.

ing characteristics of some of the reagents used to treat the wool. Water-absorption results for four reagents are given in Table IV.

Swelling Measurements

The swelling of human hair on transfer from liquid water to a picric acid solution having a *p*H 1.79 was measured. No change in length was observed for two hairs. Cross-sectional area increases of 2.2% and 2.4% were observed. The apparent molar volume of the picric acid in the aqueous solution was also determined through pycnometric measurements and found to be 123 cc/M. Both sets of measurements were made at room temperature.

Electrical-Resistance Measurements

Electrical-resistance measurements at 30°C on untreated and acid-treated wool samples are given in Table V as a function of the relative humidity of the atmosphere. Each value is an average for four fibers.

Discussion

Wool Treated with HCl

It is evident from Table II and Figures 1 and 2 that HCl has a different effect on the absorption of water by wool at high relative humidities than at low relative humidities. The change from low-humidity behavior to high-humidity behavior first becomes noticeable at 96% R.H., and results at higher relative humidities would be desirable. However, the experimental difficulties in obtaining very high relative humidities in air thermostats have already been mentioned.

Swelling experiments in which the fiber is immersed in an aqueous solution are not subject to the same experimental unreliability and can be made using solutions having high relative humidities. Only one relative humidity can be examined with swelling measurements for any given acid content, since the acid is not irreversibly held by the fiber in such an experiment. For the practical range of acid concentrations (those which do not cause hydrolytic side reactions) these relative humidities are all effectively 100%. The determination of the amount of water absorbed involves the measurement of the volume change of the fiber on being transferred from liquid water to acid solution and the measurement of the amount of acid taken up. Using these measurements

TABLE III. Absorption of Water by Untreated and Acid-Treated Silk

Reagent	Reagent Content of Sample (mM/g)	Water Uptake $\frac{mM}{g\ dry\ silk}$ at Stated Relative Humidity: Relative Humidity (%) 6.8	11.3	20.0	22.0	33.5	44.0	54.0	66.0	75.7	86.4	96.0
Untreated	—	1.54	1.86	2.48	2.74	3.42	4.12	4.80	5.49	6.56	8.10	12.0
HCl	0.12	1.50	1.78	2.41	2.42	3.29	3.92	4.61	5.24	6.29	7.75	11.4

TABLE IV. Absorption of Water by Some of the Reagents Used in the Treatment of Wool

Reagent	Water Uptake $\left[\frac{M}{M\ reagent}\right]$ at Stated Relative Humidity: Relative Humidity (%) 6.8	12.5	33.5	54.0	66.0	86.4	93.5
Orange II acid	0.48	0.94	3.41	3.49	3.65	3.99	5.19
Orange II salt	0.13	0.57	0.74	1.54	2.23	4.54	5.15
Oxalic acid	0	1.92	1.92	1.98	2.00	2.00	2.00
Picric acid	0	0	0	0	0	0.016	0.041

TABLE V. Electrical Resistance of Untreated and Acid-Treated Wool as a Function of Relative Humidity

Relative Humidity (%)	Resistance in Ohms of Samples Having Stated Treatment: Untreated	$0.75\frac{mM}{g\ wool}$ HCl	$0.81\frac{mM}{g\ wool}$ Picric Acid
60	3.39×10^{14}	1.22×10^{13}	1.37×10^{15}
84.5	3.07×10^{12}	8.23×10^{11}	1.28×10^{14}
92–93	5.45×10^{12}	9.50×10^{10}	2.10×10^{13}
96	2.64×10^{12}	5.99×10^{10}	3.63×10^{13}

and estimates of the molar volumes of the acid and water, the amount of water absorbed or desorbed as a result of the transfer can be determined.

Speakman and Stott [26] have measured microscopically the increase in swelling of wool on transfer from water to HCl solutions of various *p*H's. Values for the amount of HCl absorbed by wool as a function of the *p*H can be obtained from the work of Steinhardt, Fugitt, and Harris [30]. The apparent molar volume of HCl as a function of concentration in aqueous solutions is given by Harned and Owen [11], and the details of the calculation of amount of water absorbed are discussed by Barnard and White [3]. Calculated values of the amount of water absorbed from the solutions are given in Table VI, and one value is shown in Figure 2, where it is labeled "swelling" to distinguish it from direct measurements. The results show that there is an increase in the amount of water absorbed at the highest relative humidities.

The largest potential source of error in the calculation lies in the assumption that the apparent molal volume of the HCl inside the fiber is the same as it would be in an aqueous solution having the same ratio of acid to water. Since the apparent molal volume of HCl is relatively insensitive to concentration in aqueous solutions, it seems likely that this source of error is small. For the same reason an error in estimating the internal molarity is not very important. Furthermore, since it is probable that the H^+ ion enters into covalent bonding within the fiber, it seems likely that the estimate of the apparent molal volume of HCl is, if anything, too large. This would mean that the amount of excess water was

TABLE VI. Determination of the Amount of Water Absorbed by Wool in HCl Solutions, from Swelling Measurements

Acid Content $\left(\frac{mM}{g\ fiber}\right)$	*p*H of Treating Soln.	Total Swelling $\left(\frac{V-V_w}{V_w}\right)$	Internal Molarity $\left(\frac{M}{L}\right)$	Swelling Resulting from Acid $\left(\frac{V-V_w}{V_w}\right)$	Excess Water Absorbed $\left(\frac{mM}{g\ fiber}\right)$	$\frac{a_i}{a_w}-1$
0.75	1.0	0.060	2.11	0.0146	2.52	0.13
0.61	1.65	0.045	1.73	0.0118	1.85	0.097
0.52	1.92	0.038	1.48	0.0100	1.56	0.082
0.44	2.10	0.034	1.25	0.0084	1.48	0.078
0.21	2.75	0.022	0.604	0.0040	1.00	0.053

underestimated, thus reinforcing the argument that at the highest relative humidities the presence of HCl in the wool increases the amount of water absorbed.

Thus, the experimental results, both direct and indirect, point to two separate effects of HCl on the absorption of water by wool. The first, which is dominant except at the highest relative humidities, causes a decrease in the amount of water absorbed at a given relative humidity as compared with a similar sample which contains no acid. The second effect causes an increase in absorption of water at the highest relative humidities and can overbalance the first tendency and result in more water being absorbed by the acid-treated sample than by the untreated sample. Furthermore, the influence of the amount of acid in the sample is different at low relative humidities. At low relative humidities the amount of water absorbed at a given relative humidity decreases as the amount of acid in the sample increases. At the highest relative humidities the amount of water absorbed increases with the increase in acid content.

Wool has been shown by chemical analysis to contain one basic and one acidic sidechain for every eleven residues [12]. It has an isoionic point at *p*H 6.3 [18], and on the acid side of this will bind acid to the extent of about 0.9 meq/g, presumably by the back titration of ionized carboxylic sidechains. The value 0.9 meq/g also corresponds roughly to the amount of HCl absorbed irreversibly from the gas phase (actually the experimental value is 1.4 meq/g) [16]. Thus, when roughly 1 meq/g of HCl or less is absorbed, it is fairly well established that the H^+ ions are absorbed onto carboxyl groups, with the status of the anion as yet uncertain. All measurements given in this paper were taken with samples containing $\backsim$1 meq/g acid or less.

Wright [33] has studied the ionic mobilities of H and Br ions in horn keratin which was in contact with an HBr solution. He found that the mobility of the Br ion was several times greater than that of the H ion when the acid content of the horn keratin was below 1 meq/g and that the maximum values of the mobilities of the ions were smaller by a factor of about 1000 than corresponding values in aqueous solutions. The horn keratin-HBr system can be expected to be a reasonably close analog of the wool-HCl system.

The sigmoid absorption isotherm for water on wool and the swelling accompanying the uptake of water are well known. The large initial differential heat of absorption and the rather large amounts of water taken up at low relative humidities show that primary strong bonding sites exist within the fiber.

It is probable that at low relative humidities the polymer segments in wool are almost rigidly set in place and that diffusion through the network requires considerable activation energy. As a result it is probable that at low relative humidities the H ions of an absorbed acid are held by carboxyl groups and the anions are fixed at the basic sites within the fiber. Since the ionic sidechains are probably primary sites for water absorption, the absorbed ions can act either to block a primary site completely or to lessen its desirability as a nucleus for water absorption. In the first case, neither primary nor associated secondary absorption of water would occur at the site. This would be physically equivalent to cutting off part of the fiber, and plots such as are shown in Figures 2 and 3 would be straight lines parallel to the abscissa. In the second case, the site could serve as a center for primary absorption at some higher relative humidity, and curves such as Figures 2 and 3 would not necessarily be straight lines but would have positive slopes and would be negative over the entire range of relative humidities. In either case, the fractional decrease in absorption would be proportional to the amount of acid absorbed. The latter case would appear to apply to wool containing HCl over the low and middle ranges of relative humidity. A further possible mechanism of decreasing absorption, namely, by increasing the work of swelling by adding crossbonds, would seem to be inapplicable to the present case.

It is now necessary to consider mechanisms for increasing the absorption at high humidities. There are four possibilities: (1) production of new sites for absorption, (2) decrease in resistance to swelling, (3) hydration of absorbed ions, and (4) osmotic absorption. The first may be eliminated since there is no evidence of chemical action which might produce new sites, and no evidence, such as great swelling, of physical changes which might expose new sites. The second possibility could arise from a breaking of "salt bridges" by the absorbed acid. However, since there is no obvious reason why one acid should be more effective than another, this possibility is ruled out.

The third possibility depends on the fact that some ions are hydrated in aqueous solution and hence might be hydrated within the fiber. Evidence on the H ion can be obtained from the work of Gregor, Sundheim, Held, and Waxman [10] on ion-exchange resins. When polysulfonic acid resins were studied,

the amount of water absorbed by the resin at a given relative humidity was greater for the H form than for the K form, as would be expected from the relative hydrating tendencies of the H ion and the K ion. When resins were used which were polycarboxylic acids, the relative positions of the ions were reversed, showing that, when the H ion reacted with the carboxyl group to form the carboxylic acid, part or all of the hydrating power of the H ion was lost. Barnard, Palm, Stam, Underwood, and White [2] found that human hair containing NaBr absorbed more water at a given relative humidity than did untreated samples. Thus it would seem that the behavior of the H ion in wool is similar to its behavior in carboxylic ion-exchange resins and that there is no large contribution to absorption resulting from hydration of the H ion.

Hydration of the anion is another matter. As will be shown below, there is reason to suspect that the anion of Orange II can absorb water after the anion is absorbed by the fiber. In general, it would seem likely that, if the observed effect resulted from the hydration of the absorbed anions, it would extend over a wider range of relative humidities than is found. Although anion hydration cannot be definitely rejected, it will be provisionally rejected in favor of osmotic absorption. More results will be needed to resolve the choice of mechanism finally.

The fourth possibility, osmotic absorption, can now be examined. If the H ion is firmly absorbed by the carboxyl group and the Cl ion is not firmly absorbed, the Cl ion is free to move within the fiber but cannot leave the fiber for electrostatic reasons. As a result, water will enter the fiber to mix with and dilute the Cl ions. The system is analogous to systems involving a semipermeable membrane. The absorption of water is limited by the forces resisting swelling in the polymer network. Such a system was first used by Procter and Wilson [22] to explain the swelling of gelatin in HCl and was used by Speakman and Stott [26] to explain the swelling of wool in HCl solutions. A maximum in the curve of swelling against pH, such as is present in the wool-HCl case, is a logical result of osmotic absorption and has been cited as proof of the essential correctness of the mechanism.

Procter and Wilson assumed that both the external and internal phases were dilute aqueous solutions and applied simple equations for osmotic equilibria. Such a formulation is probably acceptable for highly swollen gelatin gels. In wool, less water is present within the fiber; and some of it, probably a sizable fraction, is absorbed on primary absorption sites and is incapable of mixing freely with Cl ions. Thus there is difficulty in knowing the "effective" internal concentration. Furthermore, the results of Wright [33] on horn keratin and of Barnard, Palm, Stam, Underwood, and White [2] on human hair have shown that ions and molecules have much less freedom of motion in keratin networks than in aqueous solutions, with the result that the dilute solution laws would not be expected to apply. Finally, except at the highest humidities, most of the Cl ions are apparently fixed on absorption sites; what might be called the precipitation of the Cl ions occurs at a relatively high activity of water apparently between 93% and 96% R.H. However, osmotic absorption is attractive qualitatively because it provides a possible explanation for the shape of the swelling against pH curve and for the fact that at very high relative humidities increasing amounts of HCl in the fiber increase the amount of water absorbed.

It might be noted in passing that some degree of mobility and freedom from absorption sites is necessary for osmotic absorption. If a fixed number of sites is available, the presence of competing species can only lower the amount of a given species absorbed at a fixed partial pressure. The distinction can be shown very simply by consideration of some work by Hill [14], who studied the adsorption of mixtures of gases which obeyed the postulates of the BET theory. At low relative pressures, where the adsorption is primarily a Langmuir adsorption process, the presence of a second gas inhibits the adsorption of the first. In the region of multilayer adsorption, where the number of adsorption sites is no longer limited, the presence of the second gas enhances the adsorption of the first.

Wool Treated with Picric Acid

The absorption of water by wool treated with picric acid differs from the absorption of water by wool treated with HCl in two ways. As is evident from Table II and Figures 1 and 2, a given amount of picric acid is more effective by almost a factor of 2 in reducing the wool's capacity for the absorption of water than is the same amount of HCl. Also, there is no difference in behavior at low and high relative humidities.

In view of the differences between HCl and picric acid, it seems likely that the picrate ion is firmly fixed on positive absorption sites within the wool at all

relative humidities. It appears that the absorbed picrate ion acts to suppress the absorption of water also. It would be expected that calculations of the amount of water taken up by the wool, using the results of swelling experiments, would indicate a decrease in the amount of water absorbed at 100% R.H. as compared with the absorption by untreated wool.

The swelling of human hair in a solution of *p*H 1.79 was found to be a 2.3% increase in volume. Steinhardt [29] gives the uptake of picric acid by wool at this *p*H as 0.89 mM/g, and the uptake by hair should be within 10% of this value, probably slightly lower [25]. The apparent molar volume of the picric acid in the treating solution (*p*H 1.79) was determined and found to be 123 cc/M. In the absence of any knowledge of the volume of the picric acid in the hair, the value in the solution was taken to be approximately correct for the hair. Using 1.32 for the density of dry hair and also for the ratio of the volumes of wet and dry hair (see Barnard and White [3]), there is a calculated volume increase of 11%, on transfer of hair from water to *p*H 1.79 picric acid solution, resulting from the uptake of picric acid alone. Any osmotically absorbed water would result in an additional volume increase. The actual result of the transfer is a 2.3% increase in volume, and this can be shown to correspond to, roughly, a 24% decrease in the amount of water absorbed. Thus, there is a calculated decrease in the amount of water absorbed, as was expected from the direct absorption results. The calculated decrease in water absorption is about the same amount as that found for wool containing 0.81 mM/g acid.

The results for picric acid in Table II are similar in character to those of Nicholls and Speakman [20]; however, in a plot such as Figure 2 their results lie below the authors'. The difference probably stems from a difference in sample preparation. Nicholls and Speakman centrifuged their samples and corrected for adhering acid, whereas the present authors washed their samples and analyzed later.

Wool Treated with Orange II Acid and Salt

Results are given in Table II for the effect of Orange II acid and Orange II salt on water absorption. Nicholls and Speakman, and Larose [17], also have used the acid form of Orange II. Their results were qualitatively similar to the present authors'.

The position of Orange II acid on plots such as Figure 1 needs some explanation. Orange II acid is more like picric acid than HCl, both with respect to its size and the *p*H at which the wool is half saturated with acid [28].

Wright [34] has very recently shown that the mobility of the Orange II acid anion is very small in horn keratin and is less than that of the H ion. Thus it would be expected to behave like picric acid with respect to water absorption. Although there is no evidence that Orange II acid becomes freed from absorption sites at high relative humidities, it does not seem able to depress the absorption of water to the extent that picric acid can. It seems possible to account qualitatively for the difference between Orange II acid and picric acid on the basis of the difference in hygroscopicity of the two dyes, as shown in Table IV, although it must be borne in mind that the absorbed dye is not in the form of crystalline particles.

It was not possible to get a large amount of Orange II salt on the wool under the conditions used. As a result, its effect on the absorption of water is small. An increase in water absorption would seem to be indicated, however, especially at the higher humidities, in agreement with results previously cited for alkali ions in hair [10] and resins [33].

Wool Treated with Other Acids

Results taken using H_2SO_4 and oxalic acid are also given in Table II. Other results taken using H_2SO_4 on wool have been reported by Das and Speakman [7], Nicholls and Speakman [20], and Larose [16]. In particular, Nicholls and Speakman give results at 98% R.H. The absorption of water by samples containing two different amounts of acid differs negligibly from the absorption by an untreated sample at 98% R.H. This suggests that osmotic swelling occurs at high relative humidities in the case of H_2SO_4. Since swelling [1] and acid uptake [27] results are available in the case of wool in H_2SO_4 solutions and apparent equivalent volumes in aqueous H_2SO_4 solutions are tabulated [15], it is possible to calculate, using swelling measurements, the amount of water absorbed. At an acidity of *p*H 2 when 0.765 meq/g of H_2SO_4 is absorbed, and the fiber diameter is increased 1.75% over the water-swollen value, there is a calculated increase in water absorp-

tion of 0.022 g water/g dry wool, or 6%, based on the regain.

In addition to the acids already discussed, Nicholls and Speakman give results for oxalic, phosphoric, monochloroacetic, dichloroacetic, and naphthalene-β-sulfonic acids. The water-absorption values at 98% R.H. for samples treated with phosphoric and monochloroacetic acids are higher than that of the untreated sample, although at lower relative humidities they are lower. For the other acids the water absorption is depressed at all humidities. This suggests that osmotic absorption occurs with phosphoric and monochloroacetic acid but not with the others. The difference between the two chloroacetic acids is particularly interesting.

Results of Resistance Measurements

Hersh and Montgomery [13] have shown that the resistance of single fibers of wool depends on the 12.6 power of the reciprocal of the weight fraction of water in the wool at 30°C. The water-absorption measurements in the tables were made at 20.5°C, but should be within 10% of comparable measurements at 30°C. Using the values at 20°C, the ratio of the resistance of an untreated sample to one containing 0.81 mM/g picric acid at 86.4% R.H. should be 40, whereas experimentally it is 4.2. Thus the picric acid and, to a much more marked degree, the HCl contributes to the conductance.

A large decrease in resistance might be expected for the HCl-treated samples between 92% and 96% R.H. or perhaps at even lower relative humidities at the increased temperature. A large decrease is found, but an equally large proportionate decrease is found for the picric acid-treated samples, so that no conclusive evidence for osmotic mixing in HCl-treated wool has been obtained from the resistance measurements.

Silk Treated with HCl

It is evident from Table III and Figure 3 that the absorption of HCl by silk decreases its capacity for absorption of water by a small constant amount. There is no sign of an increase in absorption at the highest relative humidities, and although the authors have found no swelling measurements in acid solution from which to calculate the amount absorbed at 100% R.H., there is no reason from the results to expect any osmotic absorption of water. This is somewhat surprising, in view of the behavior of wool.

Green [9] has reported that HCl has no influence on the water absorption of silk. However, his results show considerable scatter, and it is probable that his method was not sufficiently controlled to detect the small decrease. The unpublished work of Hutton mentioned previously is in essential agreement with the results in this paper.

Acknowledgment

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The Treatment of Cotton Cellulose with Aqueous Solutions of Ethylamine

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Abstract

Aqueous solutions of ethylamine from 70 to 100% amine have been investigated as to their effectiveness in reducing the crystallinity of cotton cellulose.

The degree of crystallinity of cotton cellulose was found to be little affected by ethylamine solutions containing 70% of the amine. The amine solutions of slightly higher concentration were found to strongly reduce both the crystallinity and leveling-off degree of polymerization. This reduction continued with further increase in amine concentration.

The sharp break in effectiveness at 70% ethylamine is discussed in terms of hydrogen bonding capacity in the amine-water-cellulose system.

A CONSIDERABLE amount of information has been obtained in this Laboratory on the reduction of crystallinity of cotton cellulose by treatment with anhydrous monoethylamine. In the major portion of this work which has been reported in a series of papers by Segal et al. [5, 7, 8], the amine-cellulose complex was decomposed by either extractive or evaporative removal of the amine to give cellulose of reduced crystallinity.

In the second paper of this series [7], several variables believed to have an effect on the properties of the "decrystallized cotton" were investigated. One interesting variation which was not studied in detail involves the possible reduction of crystallinity of cotton cellulose by means of aqueous solutions of the amine. Some experiments by Segal et al. [5] with a 33% aqueous amine solution indicated that the ethylamine at this strength had no effect on the cotton. At that time the effect of more concentrated aqueous solutions was not investigated.

The possibility of using aqueous solutions of ethylamine is of interest for several reasons. The anhydrous amine is a volatile liquid boiling at 17°C, thus requiring refrigeration during treatment of the cotton. Commercial ethylamine, usually furnished as a 70% aqueous solution, would not require refrigeration since its vapor pressure is only 0.566 atm at

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20°C and 0.789 atm at 30°C. The aqueous solution is shipped in standard steel drums, whereas the anhydrous product is usually shipped in heavy pressure cylinders.

The several advantages of the aqueous solution prompted an investigation of the effect on cotton cellulose of more highly concentrated aqueous ethylamine solutions.

Materials and Methods

The cellulose used throughout this present study was a low-twist singles cotton yarn purified by kier boiling. The cotton had an initial crystallinity of 90.7 ± 1.9% as determined from the kinetics of acid hydrolysis [3], with an initial degree of polymerization of 4870 as determined by cuprammonium fluidity measurements [10]. The leveling-off degree of polymerization (L.O.D.P.) according to the method of Nelson and Tripp [4] was 221 anhydroglucose units. These same methods were employed in the examination of the treated cottons.

Aqueous ethylamine solutions of 70, 75, 80, and 90% amine were prepared by adding calculated amounts of water to weighed quantities of anhydrous ethylamine. Since the reaction of water with anhydrous ethylamine is quite exothermic [6], it was necessary to add the water slowly to the precooled amine in order to avoid loss of amine during dilution.

The amine content of the aqueous solutions was determined by titration with standard hydrochloric acid. The volatile amine solutions were weighed in small, sealed, soft-glass ampoules. The ampoules, containing about 0.5 g of the solution, were broken beneath the surface of 100 ml of cooled distilled water and immediately titrated with the hydrochloric acid (methyl orange indicator).

In previous treatments of cotton with anhydrous ethylamine, chloroform usually was used for the extractive removal of the amine. For the aqueous solutions, however, it was necessary to use a solvent compatible with both the amine and the water. Acetone and methyl alcohol were found to be miscible in all proportions with the 70% ethylamine solutions. Because of the greater toxicity of methyl alcohol, acetone (reagent grade) was used in all cases for washing and extracting the amine solutions from the cotton after treatment with the aqueous solutions.

Forty-gram skeins of the air-dry cotton were immersed in the various amine solutions at 0°C under a nitrogen atmosphere and left for 4 hr. The major portion of the amine solution was then displaced from the reaction vessel by nitrogen pressure. The sample was washed with four 500-ml portions of acetone. The amine remaining in the samples was removed by Soxhlet extraction with acetone for 10 hr, after which the samples were allowed to air dry for at least 48 hr at room temperature prior to further examination.

X-ray diffraction tracings of the treated materials were obtained by means of a diffraction spectrometer operating on the focusing principle. Portions of the treated materials were ground in a Wiley mill to pass a 20-mesh screen. A thin disc specimen of ½-in. diameter and 1/16 in. thickness was prepared from 0.125 g of the resulting ground material by compression at 25,000 psi. The radial diffraction diagrams were obtained with the aid of a Geiger counter and recording potentiometer. More complete details of the instrument and sample preparation have been given in an earlier paper [8].

Results

The degree of crystallinity and L.O.D.P. of the cotton celluloses are summarized in Table I in the order of increasing concentration of the amine solutions used for treatment. In Figures 1 and 2 the data are plotted as functions of the amine concentration. It can be seen here that the cotton is little affected by treatment with 70% ethylamine. However, treatment with the amine solutions of slightly higher concentration strongly reduces both the crystallinity and the L.O.D.P., and this reduction continues with further increase in amine concentration. Finally, the rate of decrease seems to level off at the

TABLE I. Effect of Aqueous Solutions of Ethylamine on Degree of Crystallinity and L.O.D.P. of Cotton Cellulose

Amine Concentration (wt. %)	Degree of Crystallinity (%)	L.O.D.P. (Glucose Units)
Untreated control	91 ± 2	221
33*	87 ± 2*	—
70	76 ± 2	191
70	78 ± 2	200
75	46 ± 3	158
75	48 ± 4	144
80	47 ± 6	138
81	46 ± 3	143
90	26 ± 8	123
100	36 ± 12	128

* Taken from earlier work [5].

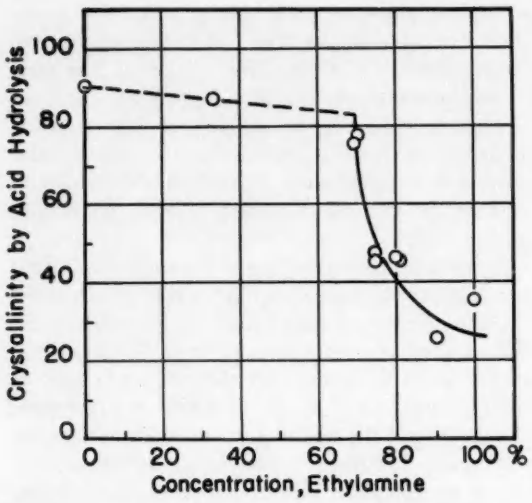

Fig. 1. Variation of crystallinity by acid hydrolysis as a function of the amine concentration of the treating bath.

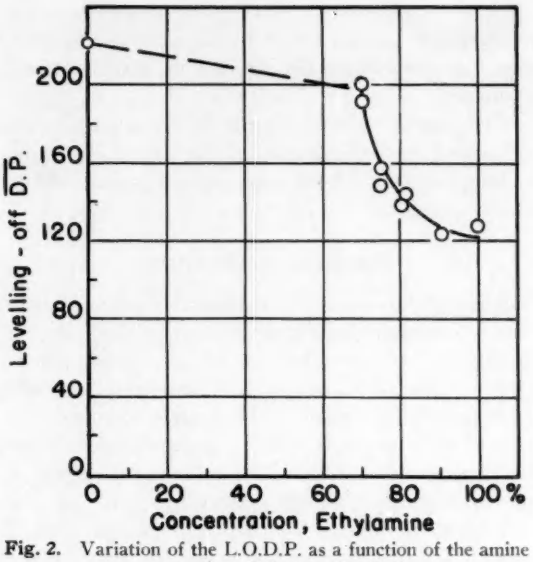

Fig. 2. Variation of the L.O.D.P. as a function of the amine concentration of the treating bath.

highest concentrations, as exhibited by the equal effectiveness of both the 90% and anhydrous ethylamine.

These results are qualitatively corroborated by the radial X-ray diffraction tracings given in Figure 3. The tracing for the cotton treated with the 70% solution is almost indistinguishable from that of the untreated cotton. A marked change is noted, however, in the diffraction tracing for the cotton treated with the 75% solution, where the strong reduction in the intensity of the 002 diffraction maxima is quite apparent. These effects are further accentuated in the series leading to anhydrous ethylamine. The diffraction tracing for the cotton treated with the 90% ethylamine is nearly identical with that given in an earlier paper [7] for the material treated with the anhydrous amine.

Discussion

All the data indicate that a minimum concentration of ethylamine slightly greater than 70% but less than 75% is required for any marked reduction in the crystallinity. In accounting for this sharp break in decrystallizing effectiveness it is necessary to consider the overall decrystallization process, i.e., cellulose to amine-cellulose complex to cellulose of reduced order. It is believed that the reduced effectiveness of the more dilute amine solutions is due to the fact that the prerequisite ethylamine-cellulose complex is not formed to any extent by ethylamine solutions containing more than 30% of water.

The presence of a critical minimum concentration is quite commonly observed in the effects of reagents on cellulose. Sodium hydroxide solutions will not produce mercerization until a certain sufficiently high concentration has been reached; sulfuric acid, cuprammonium hydroxide, and quaternary ammonium hydroxides fail to dissolve cellulose below certain rather high concentrations. According to Sisson [9], only intercrystalline swelling occurs at concentrations below that of the critical minimum, and the X-ray pattern of the native cellulose is not affected. Sisson pictures the situation as involving competitive hydrogen bonding between the cellulose and water molecules for the molecules of the complexing agent. Penetration into the crystalline regions of cellulose can occur only when there is an excess of the complexing agent over and above that amount required for hydrogen bonding with the water molecules that are present.

The break in effectiveness of the amine to alter the crystallinity therefore seems to be dependent upon a change in the ability of the amine molecules to complex with cellulose. The penetration of the amine molecules into the cellulose crystallites and the formation of the amine-cellulose complexes involves the disruption of interchain OH—O hydrogen bonds and the substitution of OH—N hydrogen

bonds involving the amino nitrogen [1]. This implies that the electron donor function of the amino nitrogens must be available for hydrogen-bond formation with the cellulosic hydroxyls. In a monoalkylamine solution containing 1 molecule of water per amine group, the hydrogen bonding potential of the nitrogen atom with respect to OH—N bond formation should be greatly reduced by complex formation with the water molecules. Hence amino nitrogens in such a solution would not be expected to enter into further hydrogen-bond formation with cellulosic hydroxyls. In an aqueous solution of ethylamine and water when the molar ratio is 1:1, the weight per cent of water is 28.6% and the amine concentration is 71.4%. According to this an ethylamine solution containing amine percentages of 71.4% or less would not be expected to enter into complex formation with cellulose. This is consistent with the experimental findings for the monoalkylamine.

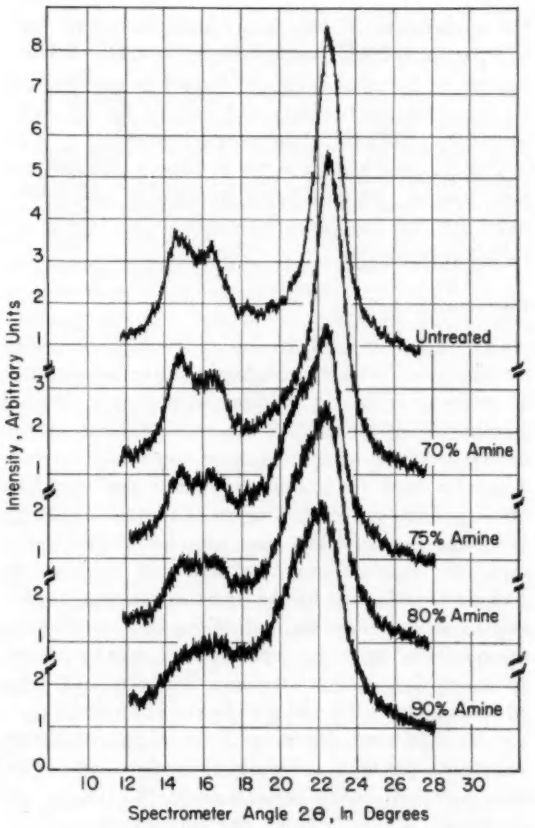

Fig. 3. Radial X-ray spectrometer tracings showing effect of aqueous ethylamine on crystalline order in cotton cellulose.

Evidence confirming this effect of water on the complexing ability of amine molecules has been obtained from another series of decrystallizations with aqueous solutions of ethylenediamine [2]. L.O.D.P. and X-ray diffraction data indicate that the minimum effective concentration for this system is slightly in excess of 60% by weight of the diamine. For a diamine molecule one would expect the OH—N bonding potential to drop sharply for a solution containing at least 2 molecules of water per molecule of diamine. For ethylenediamine this corresponds to a solution containing 62.6% diamine and 37.4% water.

The failure of the more dilute ethylamine and ethylenediamine solutions to reduce the crystallinity of cotton cellulose therefore seems to lie in their inability to form the amine-cellulose complexes prerequisite to decrystallization.

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Stress-Strain Relationships in Yarns Subjected to Rapid Impact Loading

Part I: Equipment, Testing Procedure, and Typical Results[1,2]

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Abstract

Equipment is described for elongating yarns by longitudinal impact at velocities ranging from 10 to 100 m/sec. The rate of straining at impact varies from about 100,000 to 500,000% per min.

A procedure is discussed for obtaining load-elongation curves for loading and for unloading of the specimen and for loading to rupture in a time interval of only a few milliseconds. The results of a typical loading and unloading test are presented.

Introduction

Textile materials in processing and use are subjected ever more frequently to higher rates of straining. For example, in high-speed industrial sewing the thread is subjected to impact velocities ranging from 1 to 10 m/sec as often as 5000 times per minute. This results in high-frequency cyclic accelerations of the thread which may equal several million centimeters per second per second. These high accelerations of the thread produce forces that approach, and may even exceed, the breaking strength of the thread. Similar conditions may be attained in high-speed processing of fibers, such as carding and combing or the weaving and knitting of yarns into fabrics; in the cord of an airplane tire during landing; in the safety line when a structural worker attached to it falls; and in the fabric, shroud lines, and webbing during the opening of a parachute.

The present work was undertaken to provide basic information on the behavior of textile materials when strained at very high rates; to relate the results to the molecular structure of the fibers and to the geometry of the yarns and fabrics; and finally to indicate the applications of this information to safety engineering, to industrial processing of textiles, to development of fibers of improved impact properties, and to industrial and military end uses of textile structures for specific performance requirements.

This is the first of a series of papers on rapid impact testing. In this paper equipment and procedures for this purpose are described and typical results are presented.

Historical

The stress-strain behavior of textile and other materials has been thoroughly investigated at rates of straining ordinarily referred to as "static" tensile testing. The velocity of the moving head of the testing machine in static testing is usually between about 0.1 and 10 in./min (4×10^{-5} and 4×10^{-3} m/sec). The corresponding rates of straining range from about 1 to 100% per min for textile materials. In impact testing, usually made by dropping a mass for a known height or by allowing a pendulum to swing freely through 90 to 180° to rupture the specimen, the velocity at impact is usually limited by room dimensions to values between 1000 and 20,000 in./min (0.4 and 8 m/sec). The corresponding rates of straining range from about 10,000 to 200,000% per min. Although excellent work has been published in this velocity range [13, 14, 16, 21, 23, 25–28, 30, and others], the information concerning the stress-strain behavior of textile and other materials is not as complete as that for static testing.

[1] Presented in part at the September 1953 and September 1954 meetings of The Fiber Society, and also at the November 1954 meeting of the Society of Rheology.

[2] Permission to publish this paper has been granted by the Office of the Quartermaster General, Department of the Army, which has sponsored and supported this work as a part of a broad and long-term fundamental program of research on textile materials.

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The information at higher impact velocities, 20,000 to 10,000,000 in./min (8–400 m/sec) or rates of straining ranging from about 200,000 to 100,000,000% per min, is incomplete. Much of the published work in this velocity range is theoretical or has been confined to very small strains [1–12, 15, 17–20, 22, 24, 29, 31–33, and many others]. Meredith [26] has recently published excellent stress-strain relationship data for viscose rayon, acetate, silk, and nylon yarns for rates of straining between 0.05 and 70,000% per min. The rates of straining obtainable with the equipment described in this paper are between about 100,000 and 1,000,000% per min for textile materials. Even this maximum rate of straining is considerably below the rates of straining which prevail when textile materials are tested at their critical velocities.[4] These rates of straining are estimated to range from about 10,000,000 to 100,000,000% per min.

Equipment and Testing Procedure

Equipment has been constructed at the National Bureau of Standards for applying longitudinal impacts, at velocities up to 100 m/sec, to one end of a specimen of textile fiber, yarn, or cord or other materials having similar dimensions. The rates of straining range from 100,000 to 500,000% per min. A high-speed motion picture camera and mirrors are used to photograph simultaneously the positions of the head and tail ends of the specimen during the first few milliseconds from the time of impact. The stress-strain behavior of the specimen is then derived from the photographic record.

The specimen to be tested is usually ⅔ meter long, but can be varied in length. One end is fastened to a head mass, which is impacted. The other end is fastened to a tail mass. The head and tail, with a specimen of yarn attached to them, are shown in Figure 1.

The manner of attaching the specimen is important. The specimen must not be damaged, high stress concentration must be avoided, and slippage must be minimized. An effective way of attaching a specimen is shown in Figure 1. A small hole is drilled in the end of the head mass and tail mass in such a way that it terminates in a helical groove on the surface. The bottom of the groove is coated with

[4] The concept of critical velocity was suggested by von Kármán [32, 33] and has been discussed by Hoppmann [20] and by Andersson and Steenberg [4].

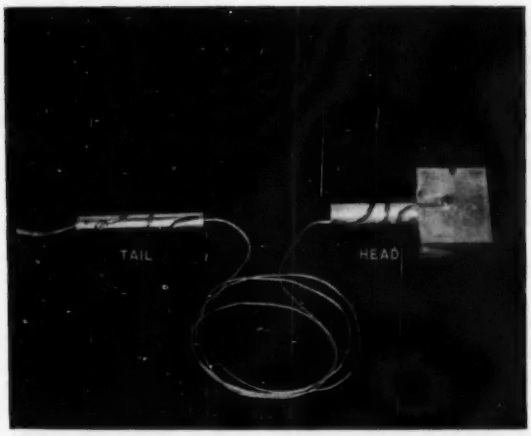

Fig. 1. Yarn specimen fastened to head and tail for an impact test.

a rubberlike high-friction compound. The end of a specimen is threaded through the hole, wound in the groove, and snubbed under the shoulder of a recessed screw. It is apparent that as the longitudinal tension in the specimen is increased during an impact test the radial pressure of the specimen against the groove is also increased. The longitudinal stress is thus effectively transferred between the specimen and the head or tail through the increased contact friction. The effective length of the specimen is equal to the distance between the inner ends of the head and tail plus 1 cm at each end for the helical groove.

The tail mass and attached specimen are inserted in a tube, as shown in Figure 2. The right portion of this tube is made of transparent plastic so that the tail mass and a portion of the specimen are visible. The head is fitted into the left end of the tube. Two

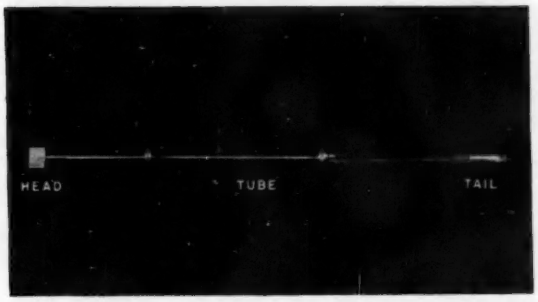

Fig. 2. Tube containing yarn specimen and attached tail mass with the head attached to left end of tube.

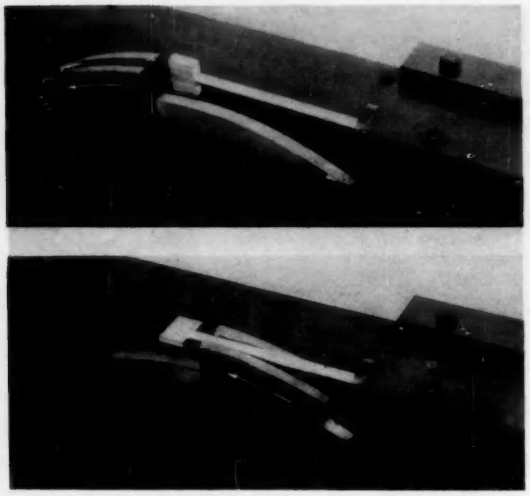

Fig. 3. Upper view shows a portion of the impact equipment with the head in a vertical position and the hammers at the instant when a contact in the triggering circuit is closed by the disk. Lower view shows the head in a horizontal position and the hammers at the instant prior to impact of the head.

disks are attached to the middle portion of the tube to serve as the bearing shaft when the tube is inserted in the impact equipment for a test.

A portion of the impact equipment is shown in Figure 3. The upper view shows the tube, with the head in a vertical position. Directly below the head and tube a portion of a heavy disk is visible. The disk can be rotated counterclockwise. Two lugs, called hammers, are attached to the disk. They are visible to the left of the head in the upper view of Figure 3. In a test the speed of the disk may be adjusted to values between 5 and 50 rps. The peripheral speed of the hammers ranges from about 10 to 100 m/sec. A stroboscope is used to measure the speed of the disk.

The upper view of Figure 3 shows the hammers in a position where a sector (not shown) attached to the disk closes an electric contact in a triggering circuit. When this circuit is closed a solenoid releases a spring-loaded cam. This cam rotates the tube containing the tail mass, specimen, and head through 90° in less time than is required for one rotation of the hammers, even when the disk rotates at a speed as high as 50 rps. With the head in a horizontal position, lower view of Figure 3, the head will be struck by the hammers of the disk for the impact test of the specimen attached to the head.

The assembly of the impact-testing equipment is shown in Figure 4. A 5-hp variable-speed motor, used for rotating the disk at high speed, is shown at the left. Directly above it is a box in which the head is caught after impact. The tube containing the head, specimen, and tail mass is shown to the right of the box. Two scales, ruled in centimeters on transparent plastic, are shown directly above the tube. Photoflood bulbs are mounted directly in back of the tube. A high-speed motion picture camera is shown in the foreground. A system of mirrors is mounted between the tube and camera. The paths of representative light beams from the head and tail are indicated by the broken lines. The mirrors are mounted on a metal base and can be readily adjusted to different horizontal positions. The mirrors can also be adjusted in their inclination so that the image of the tail and its scale appear above the image of the head and its scale in the field of view of the camera. The head and tail are photographed in silhouette, as shown in Figure 5.

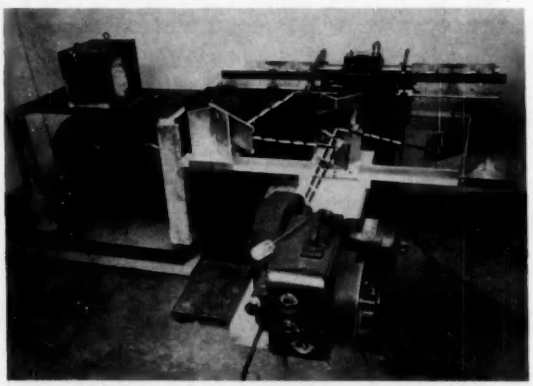

Fig. 4. Assembly of impact-testing equipment showing variable-speed motor at the left with catch box above it; high-speed camera in the foreground; photoflood bulbs, scales, tube containing head, specimen, and tail mass in the background; and mirror system in the center. Broken lines indicate paths of light beams from the head and tail.

After adjusting the speed of the disk to the desired value for a test, and with the head, specimen, and tail mass in position, the motor of the camera is turned on and, through a heavy-duty relay, the photoflood bulbs. When the film has attained the desired speed, the camera closes an electric contact in the triggering circuit of the solenoid. This contact is in series with the solenoid, a series of batteries (alternating current of 60 cycles is not reliable for this purpose), and the contact on the disk previously

referred to. The contact on the disk is closed the next time the hammers reach the position shown in the upper view of Figure 3. At this time the solenoid is energized and actuates a trigger to release the spring-loaded cam. The cam rotates the tube and head into a horizontal position, lower view of Figure 3. The head will be struck by the hammers on the next rotation of the disk for the impact test of the specimen attached to the head and tail mass. The motions of the head and tail after impact are recorded by the high-speed camera.

After impact the head is thrown to the left in Figure 4 and is caught in the box above the variable-speed motor. The tail mass is usually caught in the box. In some tests it remains in the tube or is thrown out of the rear of the plastic tube by the reaction from the specimen after rupture has occurred.

Behavior of Specimen after Impact

A few microseconds after impact the head will attain a velocity exceeding that of the hammer and therefore will move in free flight ahead of the hammer. The sudden impact of the head produces a strain in the specimen where it is attached to the head, which depends on the impact velocity and on the material being tested. This strain and a tension approximately proportional to it will be propagated along the specimen toward the tail mass. When the strain reaches the tail mass it will be reflected and the reflected strain propagated toward the head. The strain and tension at the tail mass are approximately doubled upon reflection.

The propagation of the strain along the specimen and the successive reflections at the head and the tail will continue. At each reflection the strain and the tension are increased. The increased tension at the head will cause a deceleration of the head, whereas at the tail it will cause an acceleration of the tail mass. This process will continue until the rupture strain is reached and the specimen breaks, or until the velocity of the tail equals that of the head, at which time the specimen will be at maximum average strain and under maximum average tension, but both are below the rupture values. After this time the tension in the specimen will continue to decelerate the head and to accelerate the tail mass so that the velocity of the tail will exceed that of the head. As soon as the velocity of the tail exceeds that of the head the strain will be relieved and the tension in the specimen will be decreased. This process of

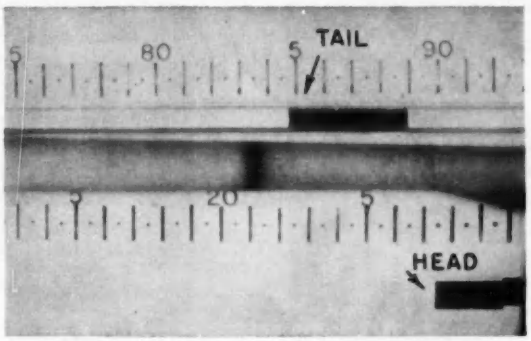

Fig. 5. Camera field view of specimen ends before impact.

strain release and propagation is probably similar to that occurring during the increase of the strain, and will continue until all the recoverable strain is relieved, at which time the tension will have been reduced to zero and the specimen will become slack. The specimen is thus loaded to a maximum tension and extension and then unloaded to zero tension and a set or extension in a total time of several milliseconds. Part of the set may be reduced by delayed recovery.

The propagation of the strain pulse after impact and subsequent reflections at the tail and head are indicated schematically by sketches *A* to *H* in Figure 6. Before impact the specimen is represented in *A* by a series of adjoining circular springs. After impact in *B* the circular spring next to the head is deformed into an ellipse and the strain pulse is indi-

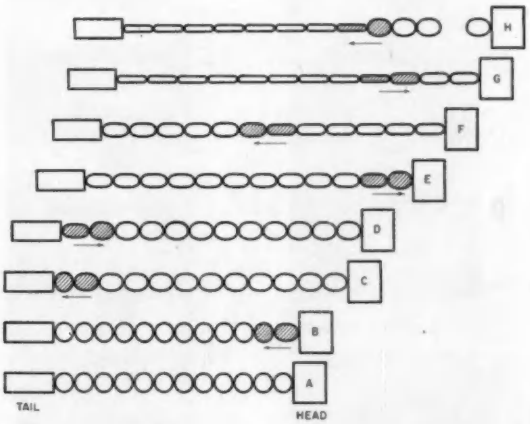

Fig. 6. Schematic representation of strain propagation in specimen, indicated by adjoining circular springs, after impact of the head at an instant between *A* and *B*. Cross-hatched circle and ellipse represent the strain pulse.

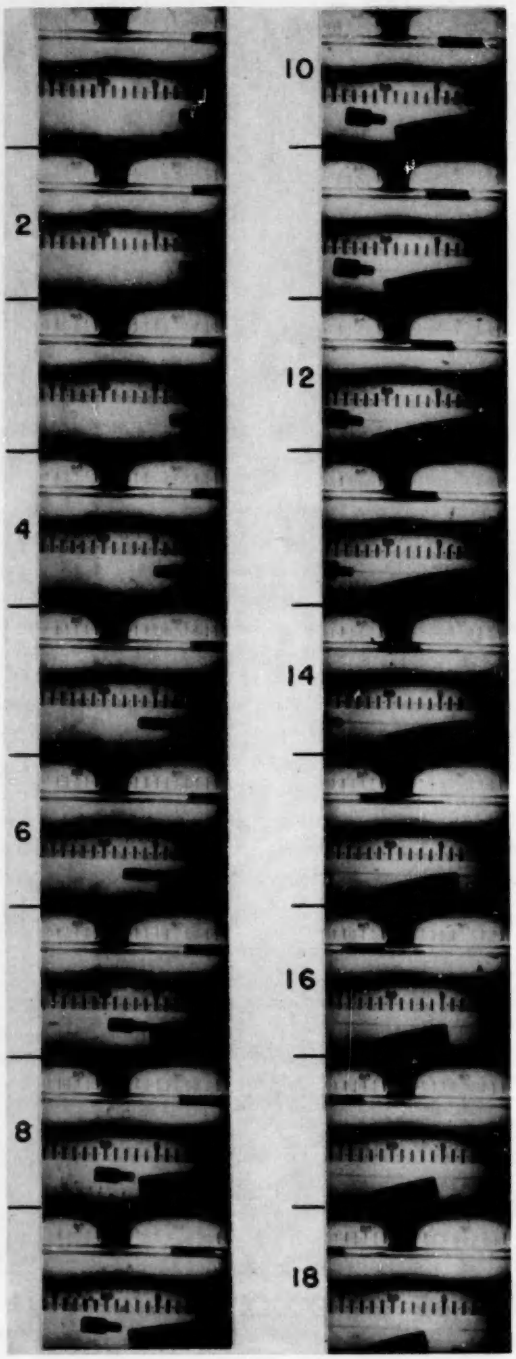

Fig. 7. Film strips showing motion of head and tail. Impact occurs between frames 2 and 3; maximum tension, between frames 10 and 11.

cated by the adjacent cross-hatched circle and ellipse. The arrow indicates the direction of strain propagation. Sketches *C* and *D* show the arrival and reflection of the strain pulse at the tail. At this moment the tail is set in motion and the ellipse before reflection is deformed to one of greater eccentricity after reflection. Sketch *E* indicates the arrival of the reflected strain pulse at the head. After reflection at the head the strain pulse is shown in sketch *F* as traveling toward the tail about midway between the head and tail. In *G* the strain pulse is shown as traveling toward the head after reflection at the tail and the high strain is indicated by the highly eccentric ellipses. After the next reflection at the head it is assumed that the rupture strain is attained and the ruptured specimen is shown in *H*. After rupture the strain is released. This condition is represented in *H* by the reconversion (recovery) of the ellipses of high eccentricity to ellipses of low eccentricity or to circles for complete recovery. The propagation of the strain-release pulse is indicated by the arrow. The ruptured end will snap toward the tail with a very high velocity and the momentum acquired by the specimen, when the strain-release pulse reaches the tail, may be sufficient to stop the tail mass or to reverse its motion.

Tests on a Nylon Yarn

A specimen of nylon yarn was fastened at one end to a head weighing 19.82 g and at the other end to a mass of 4.85 g, the length between fastenings being 65 cm. The head was impacted at a velocity of 30 m/sec.

The motions of the head and tail mass were recorded photographically by means of high-speed motion pictures taken at a rate of 2630 frames per second. The sequence of pictures is shown in Figure 7, beginning with two frames before impact, upper left-hand corner, and ending after release of the strain, lower right-hand corner. It can be seen that before impact in frames 1 and 2 the positions of the head and tail remain stationary relative to the fixed centimeter scale, which is photographed on each frame. After impact, which occurred between frames 2 and 3, the head moves relative to the fixed scale until it finally disappears from the field of view of the camera. The tail mass, on the other hand, moves very little for several frames after impact. It then speeds up until in frame 10 it moves the same amount as the head. Thereafter it moves further per frame

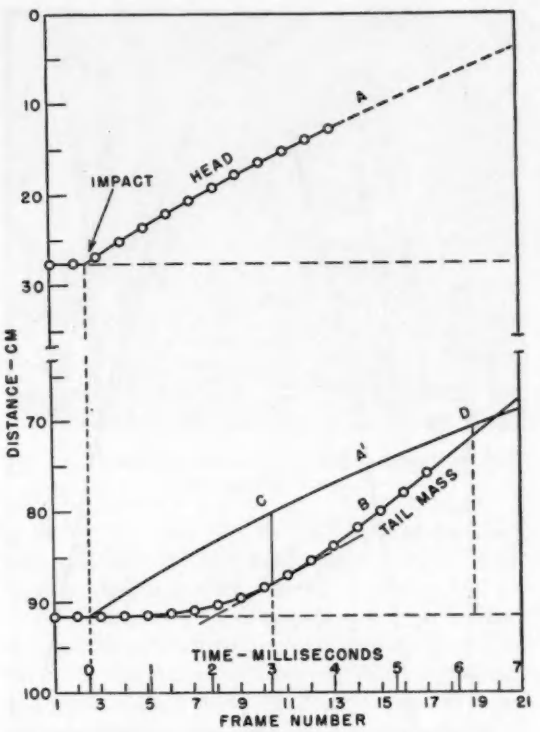

Fig. 8. Position of head and of tail mass on successive frames in an impact test of a nylon yarn.

than the head; after frame 16 the distance moved per frame is a maximum and essentially constant.

The positions of the head and of the tail on each frame were carefully measured, relative to the fixed scale, with a precision measuring micrometer. These positions are plotted in Figure 8 against frame number and also against time in milliseconds; the resulting curves will hereafter be referred to as distance-frame or distance-time curves. Zero time refers to the instant of impact and is obtained by extrapolating the distance-frame curve, *A*, of the head after impact back to the distance-frame curve of the head before impact. The point of intersection of these two curves is taken as the instant of impact.

The distance-time curve of the head is slightly concave downward, indicating that the head is slowing down. The slope of this curve at any point (time) is equal to the velocity of the head at that time. The velocity-time curve of the head is plotted in Figure 9. Immediately after impact the velocity of the head is about 45 m/sec. At 4 msec after impact it is reduced to 30 m/sec.

The distance-time curve of the tail mass, *B*, Figure 8, is concave upward, indicating that its velocity increases with time. At 3 msec the slope of the distance-time curve for the tail mass is equal to that for the head, indicating that the velocities of the head and the tail are equal. The velocity-time curve of the tail mass is also plotted in Figure 9. The velocity of the tail mass is zero before impact, then increases slowly immediately after impact. It increases most rapidly at 3 msec after impact, when it attains the head velocity of 35 m/sec. It then increases less rapidly, becoming essentially a constant, 54 m/sec, at 5 msec.

The slope of the velocity-time curve for the tail mass, Figure 9, at any point (time) is equal to the acceleration of the tail mass. This acceleration is plotted against time in Figure 10. The maximum value is more than a million centimeters per second per second. Since the force on the tail mass (and thus on the specimen at the tail) at any time is equal to the mass times its acceleration, the curve in Figure 10 is also a force-time curve of the specimen at the tail. The ordinate scale given at the right side of Figure 10 is in force units (kilograms). The curve in Figure 10 thus indicates the force that the

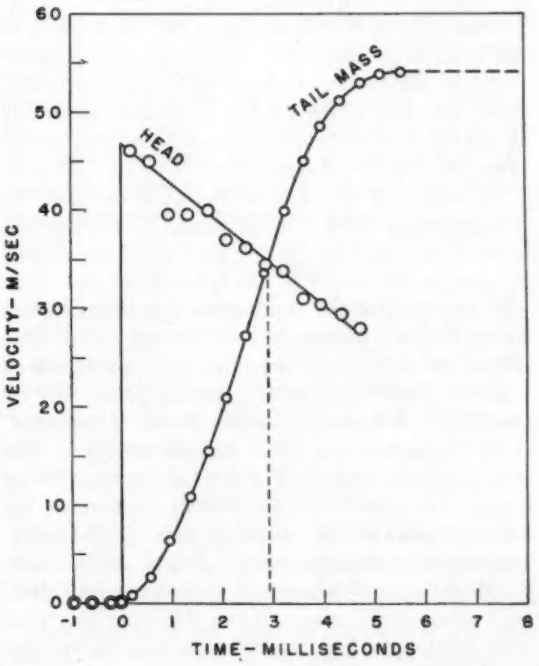

Fig. 9. Velocity of head and of tail mass after impact in a test of a nylon yarn.

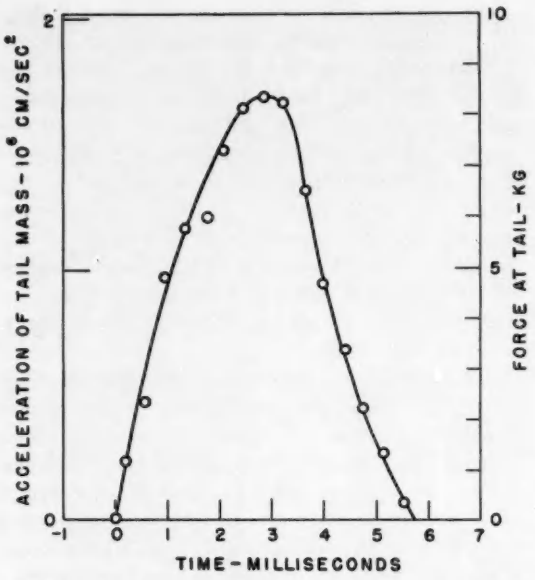

Fig. 10. Acceleration of tail mass and force at tail after impact in a test on nylon yarn.

tail mass exerts on the specimen during loading and unloading. The total time for loading and unloading is only 6 msec in this test.

From Figure 9 it is seen that the deceleration of the head at 3 msec after impact is approximately equal to one-fourth of the acceleration of the tail. Since the mass of the head is about four times that of the tail it is evident that the force at the head is essentially equal to that at the tail.

In Figure 8 the vertical distance between the distance-frame curve for the head, A, and the distance-frame curve for the tail, B, at any frame (time) is equal to the length of the specimen at that time. The extension of the specimen at any time is given by the distance between the two curves at this time minus the distance between the two curves before impact. This extension is indicated graphically by the distance between the curves A' and B, where A' is the distance-frame curve for the head, A, after it was shifted down to A' so that the portion before impact coincided with the similar portion of the curve B before impact. It can be seen that the extension (distance between curves A' and B) increases for times up to 3 msec, and then decreases. It is zero again at 6.7 msec (frame 20). At this time after impact the head and the tail have moved the

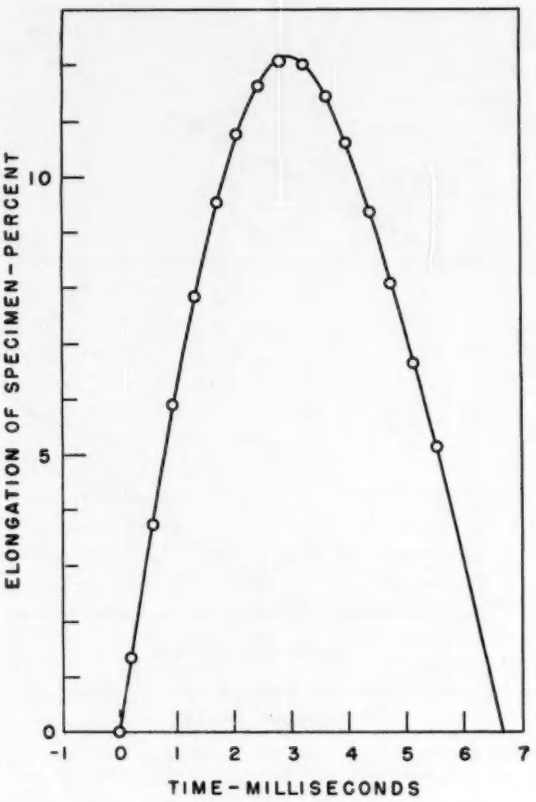

Fig. 11. Average elongation of specimen after impact in a test on nylon yarn.

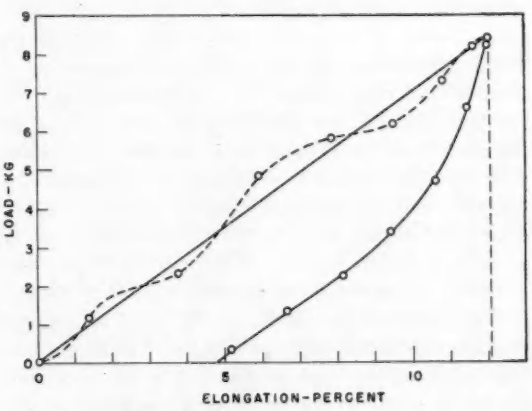

Fig. 12. Load at tail mass plotted against average elongation for loading and unloading of a nylon yarn in an impact test.

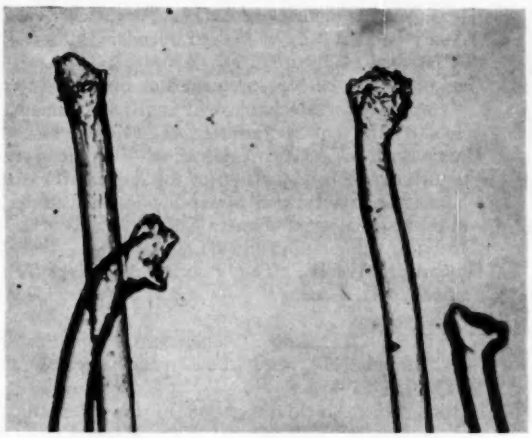

Fig. 13. Magnified view of ruptured filaments of nylon showing fused ends.

same total distance; that is, the length of the specimen (distance between head and tail) is again the same as before impact. If the specimen had recovered completely from its extension it would have been under zero strain and zero tension at this instant. It was observed, however, that the specimen was already slack in frame 19 (6.3 msec after impact). The distance between the two curves at frame 19, viz., at *D*, Figure 8, therefore, represents the extension which remained after the specimen was completely unloaded. Part of this extension may have been recovered subsequently by delayed recovery. The extension during loading and unloading, expressed as a per cent of the specimen length before impact, and termed elongation, is plotted against time in Figure 11. This elongation at any given time is the average elongation of the specimen. Actually at any given time the local elongation of the specimen is not constant, but shows a sharp increment at the strain wave front.

From the force-time curve in Figure 10 and the elongation-time curve in Figure 11 it is possible to plot simultaneous values of force and elongation. The result is a load-elongation curve for loading and also for unloading, as shown in Figure 12. The energy to maximum load is then readily obtained, as well as the energy recovered during unloading. The difference between these values, if converted into heat and assumed to be uniformly distributed throughout the specimen, would be sufficient to raise the temperature of the specimen about 10°C. Actually this hysteresis energy is not converted uniformly into heat throughout the specimen. For example, in another test in which the maximum strain was sufficient to rupture the specimen the fiber tips were fused, as shown in Figure 13, which is evidence of high heat concentration at the point of rupture. This fused condition possibly results from the relatively low heat dissipation in nylon and the high localized energy released by bond rupture.

The points for the loading curve, broken line in Figure 12, appear to lie systematically above and below the solid straight line that is drawn through them. The straight line indicates that at this high impact velocity the nylon specimen essentially obeyed Hooke's law during loading. However, the scatter of the points about the straight line is too consistent to be ascribed to experimental errors. It appears that this scattering of the points about the straight line is experimental evidence that the force at the tail mass varies in a stepwise manner. Each step in load indicates the arrival and reflection of a strain wave at the tail mass. It is significant to note that the individual points of the velocity-time curve for the head, Figure 9, show evidence that the deceleration of the head, and thus the force at the head, also varies in a stepwise manner. An analysis of these variations indicates that the time for the strain pulse to travel from the head to the tail, or 0.65 m, is about 3×10^{-4} sec. The velocity of strain propagation is therefore about 2200 m/sec. The strain at impact, given by the ratio of the velocity of the head at impact to the velocity of strain propagation, is thus about 2%. More detailed strain analyses for impact loading are given in subsequent papers.[5]

Summary

New equipment and procedures have been described for obtaining load-elongation curves of yarns at very high rates of straining. The results obtainable provide basic information about the impact properties of yarns, threads, cords, and other comparable structures.

Acknowledgment

Support for this work and permission to publish by the Office of the Quartermaster General, Department of the Army, are gratefully acknowledged.

[5] For Part II of this series, see page 529 of this issue. Part III will be published in the August issue.

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Stress-Strain Relationships in Yarns Subjected to Rapid Impact Loading

Part II. Breaking Velocities, Strain Energies, and Theory Neglecting Wave Propagation[1,2]

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Textiles Section, National Bureau of Standards

Abstract

The behavior of a yarn specimen, which is fastened at one end to a head mass and at the other end to a small tail mass, is analyzed for longitudinal impact of the specimen at the head. The analysis leads to a basic formula for "limiting breaking velocity," which is a characteristic property of the material and is independent of the dimensions of the specimen. A simple procedure is described for obtaining its value. The values for cotton, nylon, and undrawn nylon yarns tested at room temperature are found to be 130, 228, and 550 m/sec, respectively. The practical application of the limiting breaking velocity to safety engineering is shown by an example on safety lines. Formulas are derived for computing energy to any strain under impact loading and the computed values are found to agree with those obtained from the area under the impact load-extension curves.

Introduction

The first paper of this series [5] described equipment and procedures for studying the stress-strain behavior of a yarn specimen subjected to tensional impact. In a typical test, a 65-cm specimen was attached at one end to a head mass and at the other end to a tail mass. The head was impacted at velocities between 10 and 100 m/sec and subsequent behavior was recorded by high-speed photography.

The behavior of the yarn specimen after longitudinal impact is treated theoretically in this paper, neglecting wave-propagation effects. The results are compared with those obtained experimentally for several materials. The practical application of this work to safety engineering is indicated.

[1] Presented in part at the September 1953 and September 1954 meetings of The Fiber Society, and also at the November 1954 meeting of the Society of Rheology.

[2] Permission to publish this paper has been granted by the Office of the Quartermaster General, Department of the Army, which has sponsored and supported this work as a part of a broad and long-term fundamental program of research on textile materials.

Theory

Figure 1 represents a test specimen terminated by a head mass, mw, and a tail mass, nw, w being the mass of the specimen. The equations of motion of these masses will be derived and written down in terms of the following symbols.

L	length of specimen before impact
w	mass of specimen
nw	mass added at tail
mw	mass of head
x_{10}	position of tail before impact, relative to a fixed origin O
x_{20}	position of head before impact, relative to a fixed origin O
t	time after impact
x_1	position of tail at time t relative to a fixed origin O
x_2	position of head at time t relative to a fixed origin O
x_c	position of center of mass of the system at time t relative to a fixed origin O
ϵ	strain in specimen
F	force acting on specimen at time t
v_0	velocity of head immediately after impact

It is assumed here that $\frac{1}{2}w$ is concentrated at the head and the remaining $\frac{1}{2}w$ is concentrated at the tail of the specimen. Thus the problem actually

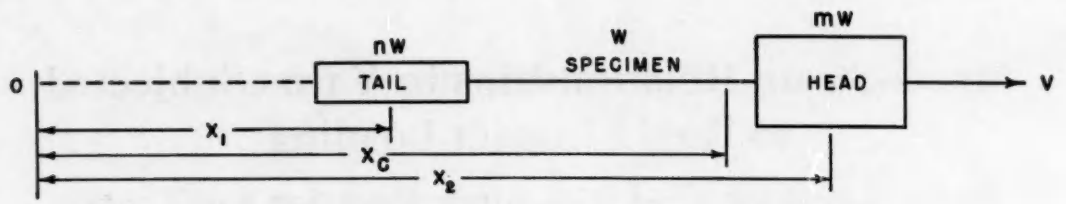

Fig. 1. Schematic drawing of test specimen for impact loading.

treated is that of a massless specimen to which a head mass $(m + \frac{1}{2})w$ and a tail mass $(n + \frac{1}{2})w$ are attached.

The force equations, neglecting air friction,[3] are:

$$F = (n + \tfrac{1}{2})w\frac{d^2x_1}{dt^2} \tag{1}$$

$$F = -(m + \tfrac{1}{2})w\frac{d^2x_2}{dt^2} \tag{2}$$

From definition of the center of mass we obtain:

$$(n + \tfrac{1}{2})wx_1 + (m + \tfrac{1}{2})wx_2 = (n + m + 1)wx_c$$

Differentiating and eliminating w gives:

$$(n + \tfrac{1}{2})\frac{dx_1}{dt} + (m + \tfrac{1}{2})\frac{dx_2}{dt} = (n + m + 1)\frac{dx_c}{dt} \tag{3}$$

Since $\epsilon L = (x_2 - x_1) - (x_{20} - x_{10})$ we obtain by differentiation:

$$\frac{dx_1}{dt} - \frac{dx_2}{dt} = -L\frac{d\epsilon}{dt} \tag{4}$$

Solving equations (3) and (4) for dx_1/dt and dx_2/dt gives:

$$\frac{dx_1}{dt} = \frac{dx_c}{dt} - \frac{(m + \frac{1}{2})L}{n + m + 1}\frac{d\epsilon}{dt} \tag{5}$$

$$\frac{dx_2}{dt} = \frac{dx_c}{dt} + \frac{(n + \frac{1}{2})L}{n + m + 1}\frac{d\epsilon}{dt} \tag{6}$$

At maximum strain $\epsilon = \epsilon_m$ and $d\epsilon/dt = 0$, and therefore:

$$\frac{dx_1}{dt} = \frac{dx_2}{dt} = \frac{dx_c}{dt} \quad (\epsilon = \epsilon_m) \tag{6a}$$

That is, for a typical loading and unloading test under impact conditions the velocity of the tail mass at the instant of maximum strain is equal to the velocity of the head and both are equal to the velocity of the center of the total mass. Since the total momentum imparted by the hammer to the head immediately after impact is $(m + \frac{1}{2})wv_0$, it follows from conservation of momentum that:

$$\frac{dx_c}{dt} = \frac{(m + \frac{1}{2})v_0}{n + m + 1} = \text{Constant} \tag{7}$$

which is also the velocity of the head and of the tail mass at maximum strain. The velocity of the head, therefore, decreases from v_0 immediately after impact to $[(m + \frac{1}{2})v_0]/(n + m + 1)$ at the time of maximum strain. It is seen that this decrease is equal to $[(n + \frac{1}{2})v_0]/(n + m + 1)$ and thus depends upon the values of n and m.

From equations (5) and (1), or (6) and (2), it follows that

$$\frac{d^2\epsilon}{dt^2} = -\frac{n + m + 1}{(n + \frac{1}{2})(m + \frac{1}{2})}\frac{F}{Lw} \tag{8}$$

Integration gives

$$\left(\frac{d\epsilon}{dt}\right)^2 = -\frac{2}{Lw}\frac{n + m + 1}{(n + \frac{1}{2})(m + \frac{1}{2})} \times \int_0^\epsilon F\,d\epsilon + C \tag{9}$$

at $t = 0$, $\epsilon = 0$, and $d\epsilon/dt = v_0/L$. Therefore $C = v_0^2/L^2$ and:

$$\left(\frac{d\epsilon}{dt}\right)^2 = \frac{v_0^2}{L^2} - \frac{2}{Lw}\frac{n + m + 1}{(n + \frac{1}{2})(m + \frac{1}{2})} \times \int_0^\epsilon F\,d\epsilon \tag{10}$$

At maximum strain $\epsilon = \epsilon_m$ and $d\epsilon/dt = 0$. It follows, therefore, that:

$$\log v_0 = -\frac{1}{2}\log\frac{(n + \frac{1}{2})(m + \frac{1}{2})}{n + m + 1} + \log\sqrt{\frac{2L}{w}\int_0^{\epsilon_m} F\,d\epsilon} \tag{11}$$

[3] The force on the tail mass, due to air friction, was calculated to be approximately 1% of the yarn tension.

In an impact test the specimen will break if the impact velocity v_0 is large enough that the rupture strain ϵ_r is attained. The minimum breaking velocity v_n for a given n is the velocity just sufficient to cause the specimen to break when $\epsilon_r = \epsilon_m$.

Under these conditions we have:

$$\log v_n = -\frac{1}{2}\log\frac{(n+\frac{1}{2})(m+\frac{1}{2})}{(n+m+1)} + \log\sqrt{\frac{2L}{w}\int_0^{\epsilon_r} F\,d\epsilon} \quad (12)$$

Equation (12) expresses the minimum breaking velocity as a function of n. If ϵ_r and the shape of the stress-strain curve are both independent of the rate of straining, the expression under the radical sign is a constant having the dimensions of velocity squared. At high rates of straining the value of ϵ_r is less than that obtained at conventional testing rates. Also, the slope of the stress-strain curve is greater at higher rates of straining. However, for rates of straining of the same order of magnitude, these changes are small, and their effects compensate each other. Consequently, the area under the stress-strain curve should be essentially constant for the rates of straining considered here. Under these conditions a plot of $\log v_n$ vs $\log[(n+\frac{1}{2})(m+\frac{1}{2})/(n+m+1)]$ would be a straight line of slope $-\frac{1}{2}$.

By extrapolating from impact test data to the point at which $\log[(n+\frac{1}{2})(m+\frac{1}{2})/(n+m+1)] = 0$ a characteristic velocity v_b is obtained, viz.,

$$v_b = \sqrt{\frac{2L}{w}\int_0^{\epsilon_r} F\,d\epsilon} \quad (13)$$

If we let ρ = density of the specimen and σ = stress, equation (13) reduces to the form

$$v_b = \sqrt{\frac{2}{\rho}\int_0^{\epsilon_r} \sigma\,d\epsilon} \quad (14)$$

It is thus seen that v_b is a quantity characteristic of the material itself except for a possible dependence on the rate of straining.

Equation (14) can be rearranged in the form:

$$\tfrac{1}{2}\rho v_b^2 = \int_0^{\epsilon_r} \sigma\,d\epsilon \quad (15)$$

which states that the kinetic energy density in the specimen when traveling at the velocity v_b is just equal to the strain-energy density required to break the specimen. We thus see that, if the specimen is impacted at a velocity greater than v_b, it will always be broken. For this reason we call v_b the limiting breaking velocity.

Von Kármán derived a critical velocity, v_c, [6] at which a filament will break immediately upon impact.

$$v_c = \int_0^{\epsilon_r} \sqrt{\frac{1}{\rho}\frac{d\sigma}{d\epsilon}}\,d\epsilon \quad (16)$$

This equation was obtained from a consideration of plastic and elastic wave propagation in a material for which the stress-strain curve is concave downward, and the stress is independent of the rate of straining.

The results calculated from equations (14) and (16) differ slightly. However, in the special case when Hooke's law is obeyed both equations (14) and (16) reduce to:

$$v' = \epsilon_r\sqrt{E/\rho} \quad (17)$$

This formula may be expressed in terms of the more familiar textile quantities of tenacity and per cent elongation at rupture, viz.,

$$v' = 29.7\sqrt{\text{Tenacity (g/den)} \times \text{Elongation (\%)}} \quad (18)$$

where the unit for v' is meters per second.

Meredith [1] has obtained evidence that at high rates of straining the load-extension curves of some materials become more Hookean. These formulas thus assume considerable importance and by means of equation (18) estimates of the critical velocities of yarns may be computed from their tenacities and elongations at rupture under impact-testing conditions.

In a subsequent paper [4] the behavior of the specimen after longitudinal impact is treated by a theory which considers the effects of wave propagation. This treatment shows that the results given in this paper for nonwave theory are valid when the tail mass is greater than $40w$. For tail masses less than $40w$ the effects of wave propagation may become appreciable and must be considered in the theoretical treatment.

Experimental Results

Experimental values of v_n corresponding to different values of n were obtained on a number of different materials. These values of $\log v_n$ are plotted in

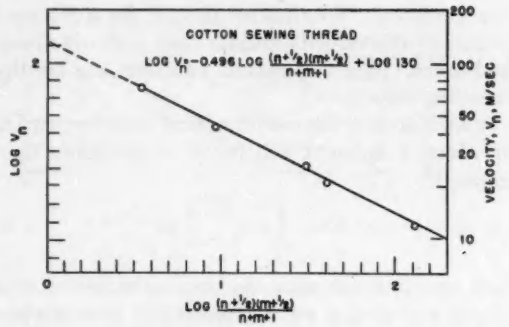

Fig. 2. Relationship between impact velocity to rupture, v_n, and head-tail mass parameter, $[(n + \frac{1}{2})(m + \frac{1}{2})]/(n + m + 1)$, for cotton sewing thread.

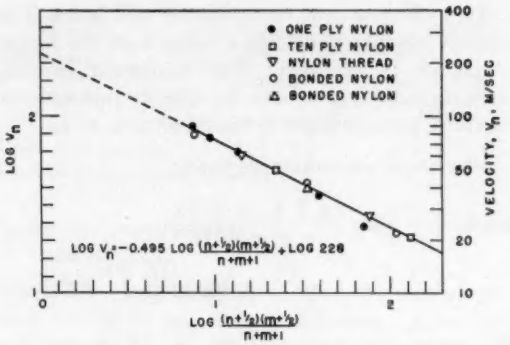

Fig. 3. Relationship between impact velocity to rupture, v_n, and head-tail mass parameter, $[(n + \frac{1}{2})(m + \frac{1}{2})]/(n + m + 1)$, for nylon yarns and threads.

Figures 2, 3, and 4 against $\log [(n + \frac{1}{2})(m + \frac{1}{2})/(n + m + 1)]$. These plots are straight lines having the following empirical equations:

For cotton thread:

$$\log v_n = -0.496 \log \frac{(n + \frac{1}{2})(m + \frac{1}{2})}{n + m + 1} + \log 130$$

For nylon yarn and threads:

$$\log v_n = -0.495 \log \frac{(n + \frac{1}{2})(m + \frac{1}{2})}{n + m + 1} + \log 228$$

For undrawn nylon:

$$\log v_n = -0.500 \log \frac{(n + \frac{1}{2})(m + \frac{1}{2})}{n + m + 1} + \log 550$$

It should be noted that the slope of each line represented by these equations is very close to $-\frac{1}{2}$ in accordance with equation (12) for $\log v_n$.

Design of Safety Lines

The empirical equation derived for $\log v_n$ has many practical applications. Consider, for example, a safety line of length L which connects a construction worker to a rigid point of the structure. Under these conditions m is infinite. The maximum free fall of the worker would be $2L$ and the maximum free fall velocity $2\sqrt{gL}$. As m becomes infinite equation (12) reduces to

$$\log v_n = -\tfrac{1}{2} \log (n + \tfrac{1}{2}) + \log v_b \qquad (19)$$

Making the assumption (which must be checked by experiment) that the safety line behaves under impact like the single yarn considered in the derivation of equation (19), substituting $v_n = 2\sqrt{gL}$ and solving for n, one obtains:

$$n = \frac{v_b^2 - 2gL}{4gL}$$

If v_b is 200 m/sec for the material of the safety line, L = 10 m, and g = 9.8 m/sec^2, the computed value of n is 101. If the weight of the worker nw is 202 lb, the minimum weight of 10 m of safety line w to just support the worker at impact is 2 lb according to this computation.

This weight is approximately that of a rope 1/2 in. in diameter [2]. A nylon rope 7/16 in. in diameter has a static breaking strength of 4000 lb [3] or twenty times the weight of the worker. However, under the dynamic conditions just assumed a nylon rope with v_b = 200 m/sec would have no factor of safety whatever according to this computation.

If v_b for the material of the safety line is 100, n = 25, and for the same weight of worker w would

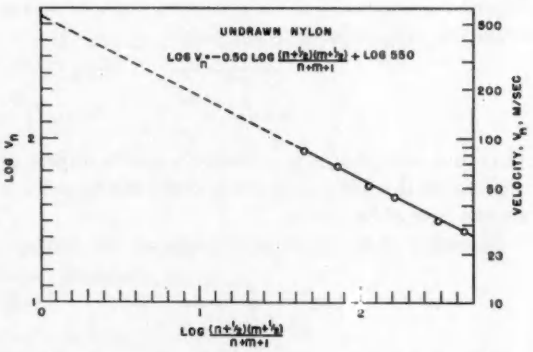

Fig. 4. Relationship between impact velocity to rupture, v_n, and head-tail mass parameter, $[(n + \frac{1}{2})(m + \frac{1}{2})]/(n + m + 1)$, for undrawn nylon.

have to be 8 lb. This weight is approximately that of a rope about 1 in. in diameter [2]. A manila rope 1 in. in diameter has a static breaking strength of 11,000 lb, or fifty times the weight of the worker. Again, under dynamic conditions, this manila rope would not provide a reasonable factor of safety according to this computation. Results obtained by Newman [3] showed that a 9/16-in. diameter sisal rope 10 ft long broke when a weight of 142 lb was dropped a height of only 20 ft.

Energy of Straining

The energy per unit length, Q, to stress the specimen to a strain ϵ is given from equation (10) by the equation:

$$Q = \int_0^{\epsilon} F\,d\epsilon = \frac{Lw}{2}\,\frac{(n+\tfrac{1}{2})(m+\tfrac{1}{2})}{n+m+1} \times \left[\left(\frac{v_0}{L}\right)^2 - \left(\frac{d\epsilon}{dt}\right)^2\right] \quad (20)$$

where $d\epsilon/dt$ is the slope of the strain-time curve at the strain ϵ. If the specimen is not ruptured but is loaded to a maximum strain, ϵ_m, and then unloaded the energy, Q_m, to the maximum strain, ϵ_m, is given by the equation:

$$Q_m = \int_0^{\epsilon_m} F\,d\epsilon = \frac{Lw}{2} \times \frac{(n+\tfrac{1}{2})(m+\tfrac{1}{2})}{n+m+1}\left(\frac{v_0}{L}\right)^2 \quad (21)$$

since $(d\epsilon/dt)_{\epsilon=\epsilon_m}$ is zero. If the specimen is ruptured, the energy, Q_r, to the rupture strain, ϵ_r, is given by the equation:

$$Q_r = \int_0^{\epsilon_r} F\,d\epsilon = \frac{Lw}{2}\,\frac{(n+\tfrac{1}{2})(m+\tfrac{1}{2})}{n+m+1} \times \left[\left(\frac{v_0}{L}\right)^2 - \left(\frac{d\epsilon}{dt}\right)^2_{\epsilon=\epsilon_r}\right] \quad (22)$$

The value of $(d\epsilon/dt)_{\epsilon=\epsilon_r}$ will be zero if the impact velocity of the head is just sufficient to produce rupture. Above this velocity $(d\epsilon/dt)_{\epsilon=\epsilon_r}$ is a positive quantity.

By means of equations (20), (21), and (22) it is possible to compute Q, Q_m, and Q_r from the conditions of a test. For Q_m it is only necessary to know the velocity, v_0, of the head at impact. For Q and Q_r the value of $d\epsilon/dt$ and $(d\epsilon/dt)_{\epsilon=\epsilon_r}$ must be known in addition to the value of v_0. The values of v_0, $d\epsilon/dt$, and $(d\epsilon/dt)_{\epsilon=\epsilon_r}$ are readily obtained from the positions of the head and of the tail on the high-speed motion pictures taken during the test. The energy values computed by means of these equations for different materials and impact testing conditions are plotted in Figure 5 against those derived from the area of the impact load-extension curves. The plotted points fall near a straight line having a slope equal to 1.

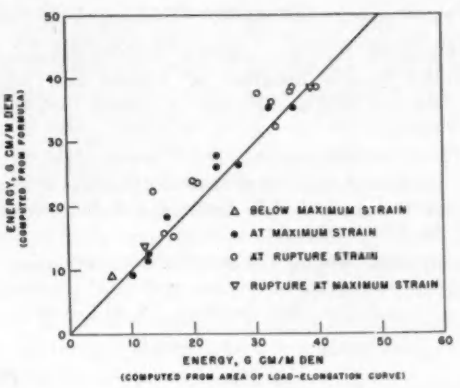

Fig. 5. Energy values computed from formulas plotted against those based upon area of the impact load-extension curves.

Summary and Conclusions

The theoretical treatment given in this paper for longitudinal impact of a yarn leads to a formula for the limiting breaking velocity that is a characteristic property of the material and is independent of the dimensions of the specimen. A specimen impacted at a velocity greater than its limiting breaking velocity will always be broken. A simple procedure is described for obtaining this limiting breaking velocity from impact test data, and results are given for cotton, nylon, and undrawn nylon yarns. The potential importance of the limiting breaking velocity to safety engineering is indicated by its application to estimates of margin of safety of rupture of safety lines by construction workers. The theoretical treatment also leads to formulas for obtaining energy to any given strain, including rupture strain, under different impact conditions. These values agree reasonably well with those obtained from the area under the impact load-extension curves.

Acknowledgment

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Effect of Kiering on the Crystallinity of Cotton Cellulose

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Abstract

Although kier boiling is a common commercial treatment applied to cotton, its effect on the crystallinity of cotton cellulose apparently has not been investigated.

In the present work, the effect on the crystalline-amorphous ratio of a laboratory kiering and of alcohol extraction and boiling in water under pressure has been studied. Acid-hydrolysis crystallinity determinations and moisture-sorption measurements on three varieties of cotton have indicated (1) that standard purification treatments can increase the crystallinity of raw cotton; (2) that the extent of crystallization varies with the individual sample; and (3) that the crystallinity values reported in the literature for purified cottons are probably higher than those for native cottons because of the changes induced by the purification treatments.

ALTHOUGH kier boiling is a common commercial treatment applied to cotton for removing most of the noncellulosic constituents, its effect on the crystalline-amorphous ratio of cotton cellulose apparently has not been investigated.

The crystallinity of cellulose from various sources has been studied by several physical and chemical methods, and the existing data have been reviewed and summarized by Nickerson [12] and Ward [21]. Crystallinity determinations on cotton cellulose have usually been made after purification treatments equivalent to kiering; therefore little is known about the quantity of crystalline material present before such treatment. Nelson and Conrad [10] have published data on two specially selected atypical samples (a very immature cotton and Arkansas "green lint" cotton) and one normal cotton before and after various laboratory purification treatments. The results showed an insignificant increase in crystallinity by the normal cotton but an appreciable gain by the atypical cottons after hot aqueous treatments. They commented on this increase but concluded at that time that the preliminary alkali extraction did not significantly affect the percentage of crystalline material. It should be noted that conclusions drawn from data on such unusual material would not necessarily apply to the cottons of commerce.

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

Recently, the crystallinity of 7 different varieties of raw cotton (as determined by an acid-hydrolysis method [10, 13]) was found to range from 73 to 83% as compared with a range of 82 to 88% reported earlier [13] for another series of raw cottons. By contrast, 2 samples of kiered cotton were found to be 91% crystalline, a value appreciably above those just cited for raw cottons. This prompted an investigation of the crystallinity after kiering of 3 samples selected from the recent series of 7 cotton varieties.

Materials and Methods

Three varieties of cotton, Stoneville 2B, Deltapine 14, and S × P, were chosen for study. The unpurified cottons were in the form of loose-twist 16/2's yarn. Maturity, as determined by ASTM methods and reported elsewhere [5], was 74% for Stoneville 2B, 74% for Deltapine 14, and 86% for S × P. Wax content was about 0.6% for all 3 varieties.

Three purification treatments were applied to the above yarns: kiering, "pressure boiling," and alcohol extraction. Kiering was performed in the laboratory by heating skeins of yarn in 1% sodium hydroxide solution at 5-lb gage pressure for 6 hr (temperature, approximately 108°C). "Pressure boiling" was done in the same way, except that the skeins were immersed in distilled water instead of alkali solution. Alcohol extraction of 2-hr duration was carried out with 95% ethanol in a Soxhlet apparatus.

Crystallinity was determined by following the kinetics of hydrolysis in 6 *N* hydrochloric acid at 100°C, using the modified procedure previously described [10]. Values were corrected to a "total cellulose" basis, making allowance for moisture and noncellulosic constituents. Cellulose content was determined by the ethanolamine-extraction method of Kettering and Conrad [9] where isolated cellulose was weighed after washing and drying. The leveling-off degree of polymerization (hereafter abbreviated as L.O.D.P.), which is believed to be an indication of crystallite length [11], was determined by hydrolyzing 2-g samples at 80°C for 4 hr in 2.5 *N* hydrochloric acid and measuring the fluidity of dispersions of the dried hydrocelluloses by methods in use at this Laboratory [2, 19]. The material was dispersed (at 0.5 g/dl) in cuprammonium hydroxide, and the intrinsic viscosity of the dispersion, as given by the formula $[\eta] = 1.70(\eta_{sp})^{0.694} - 0.160$, was multiplied by the factor 260 to obtain the degree of polymerization.

Moisture-regain data were obtained by exposing 0.5-g samples, previously dried in vacuum at 60°C, to atmospheres of constant relative humidity maintained by saturated salt solutions in closed desiccators. These were kept in a constant-temperature room at 21±1°C (70±2°F). According to Wink and Sears [22] the following relative humidities are obtained at this temperature with the respective saturated salt solutions: lithium chloride, 11.1% R.H.; potassium acetate, 23.0% R.H.; magnesium chloride hexahydrate, 33.0% R.H.; and potassium carbonate, 43.9% R.H. Of these, only the potassium acetate solution has an appreciable temperature coefficient, 0.075%/°F.

Values of relative humidity between 11 and 44% R.H. were chosen in order that the data might be used to calculate internal surface areas by the Brunauer-Emmett-Teller (BET) equation [1]. This choice was based on a study by Rowen and Blaine [16], who obtained sorption isotherms from 3.4 to 96.8% R.H. for various textile fibers but found that only the regain data below 47% R.H. were suitable for surface-area calculations since the BET plots depart from linearity above this value.

Results and Discussion

The crystallinities of the cottons before and after purification treatments are given in Table I. It is apparent that the values for untreated cottons are appreciably below the range of crystallinity generally attributed to cotton cellulose. The value for S × P cotton before kiering is unusually low. In an attempt to explain this very low value, the percentages of noncellulosic constituents of the 3 cotton varieties before kiering were examined (see Table II). This sample had 0.8% and 0.4% more noncellulosic sub-

TABLE I. Effect of Various Purification Treatments on the Crystallinity of Some Cottons as Determined by Acid Hydrolysis

Variety	Acid-Hydrolysis Crystallinity*			
	Untreated (%)	Alcohol-Extracted (%)	"Pressure-Boiled" (%)	Kiered (%)
Stoneville	78 ± 5	90 ± 2	90 ± 3	93 ± 2
Deltapine	80 ± 5	79 ± 2	85 ± 4	85 ± 3
S × P	72 ± 2	79 ± 4	84 ± 4	84 ± 3
Unknown (commercial yarn)	84 ± 2	—	—	91 ± 2

* Values are intercepts with standard errors, based on 15–20 observations.

TABLE II. Percentages of Noncellulosic Material in Yarns before and after Treatment

Variety	Noncellulosic Material (Oven-Dry Basis)			
	Untreated (%)	Alcohol-Extracted (%)	"Pressure-Boiled" (%)	Kiered (%)
Stoneville	5.5	2.5	2.4	0.8
Deltapine	5.9	2.2	2.7	0.6
S × P	6.3	3.5	3.5	1.1

stances, respectively, than the Stoneville and Deltapine samples. It is possible that the presence of excess noncellulosic material in S × P cotton could have been effective in decreasing the crystallization of the cellulose in this sample at the time of initial drying of the fibers (that is, during opening of the cotton boll). The amounts of noncellulosic materials present after the various purification treatments are given in Table II. The somewhat greater amount in S × P is seen to persist after all treatments.

Upon examining the crystallinity values after treatment (Table I), it is at once apparent that kiering produced an increase in crystallinity for all 3 varieties. The magnitude of this increase varied from only 5% for Deltapine, which is below the level of statistical significance, to 12% for S × P and 15% for Stoneville, both of which are significant at a probability of less than 1%. Boiling under pressure brought about essentially the same results as kiering, but alcohol extraction produced varying results on the 3 varieties. The crystallinity of Stoneville cotton was increased as much by alcohol extraction as by kiering or "pressure boiling"; the crystallinity of Deltapine remained unchanged, while that of S × P was intermediate between the values for the untreated and the "pressure-boiled" or kiered material.

In considering the greater improvement in fine-structural organization resulting from kiering and "pressure boiling" as compared to alcohol extraction, it is pertinent to examine the amount (Table II) and kind of noncellulosic material removed. Hot alcohol extracts wax and small amounts of other noncellulosic materials. Boiling in water under pressure removes water-soluble sugars, some organic acids, inorganic ash, and possibly some of the wax. Since "pressure boiling" raises the temperature above the melting point of the wax (approximately 77°C), the melted wax could presumably change its location in the fiber. Kiering effectively removes pectic material, water-soluble organic and inorganic constituents, proteins, and most (but not all [6]) of the wax. The superiority of kiering and "pressure boiling" in causing crystallization of native cotton is not necessarily due to more complete extraction of noncellulosic materials from the cotton, since "pressure boiling" caused practically the same crystallinity increases as kiering, yet did not remove the noncellulosic materials as completely. The chief factors involved in increasing the crystallinity are believed to be the plasticizing action of water and the effect of heat in increasing the mobility of the long-chain molecules. These ideas have been expressed by Steurer [18], who studied the "recrystallization temperatures" of cellulose and cellulose ethers. For cellulose he found that the temperature at which recrystallization takes place is lowered from above the decomposition point (above 200°C) to about 100°C when normal moisture regain is present and to an even lower temperature (about 60°C) when the material is wet with liquid water. This perhaps would explain the erratic effects of alcohol extraction. During this purification process the fiber is exposed to a small amount of water—the 5–7% normally present in air-dry cotton and the water present in 95% ethanol—and to moderate heat (about 70–75°C), which is just on the borderline of Steurer's "freezing temperature" for cellulose. Thus, in the case of Stoneville cotton, practically complete conversion of metastable amorphous to crystalline cellulose took place, while in the other two cases less conversion was accomplished.

The L.O.D.P. values of the cottons after various treatments are given in Table III. L.O.D.P. values were not determined on the unpurified yarns because the wax present prevented the acid from wetting the yarns at the temperature at which the hydrolysis was carried out. If this wax was removed by alcohol extraction, the yarns were uniformly and completely wetted. To determine if this treatment affected the L.O.D.P., one sample was caused to "wet out" by adding a wetting agent to the acid; a parallel sample was extracted with alcohol before hydrolysis. Comparison of the L.O.D.P. values (226 with wetting

TABLE III. Leveling-Off Degree of Polymerization of Cottons after Various Pretreatments

Variety	Alcohol-Extracted	"Pressure-Boiled"	Kiered
Stoneville	220, 212	210	212
Deltapine	224, 216	210	213
S × P	220, 217	219	210

agent, 220 after alcohol extraction) indicated that the alcohol extraction caused no change in L.O.D.P. within the error of measurement; therefore the remainder of the samples were extracted before hydrolysis. Using the alcohol-extracted samples as controls, it is seen that the L.O.D.P.'s were not changed by any of the treatments within the error of measurement (±5%). Although the L.O.D.P. is believed to be closely related to the crystallite length, the fact that its value did not change with increasing crystallinity does not necessarily give a clue to the location of the new ordered regions. Three possibilities exist: (1) extension of crystallites at the ends, (2) increase in thickness or lateral dimensions of the crystallites, and (3) formation of new crystalline areas, not attached to existing crystallites. Any combination of these locations may also occur. If the growth occurred only at the crystallite ends, the L.O.D.P. should change, but, if new short crystallites were simultaneously formed in the amorphous regions, their presence could nullify this effect. It should be pointed out, however, that because the viscometrically determined degree of polymerization approaches a weight average the proportion of short micelles would have to be rather large to effect a detectible change in the average D.P. This precludes the possibility of detecting formation of new crystalline areas unless fractionation studies are undertaken.

Lateral growth of crystallites seems the most attractive postulate on the basis of Frey-Wyssling's recently proposed model of the fine structure of cellulose [4]. In this model, the elementary fibrils (the units of which the microfibrils are constructed and which contain the crystallites) consist of a crystalline core flattened parallel to the 101 lattice plane and embedded in a cortex of paracrystalline (less well-ordered) cellulose. Since the tendency toward aggregation in the 101 plane is greater than perpendicular to it, water may be occluded between 101 planes during the formation of the microfibrils in the growing plant. This water is strongly bonded to the cellulose chains. Subsequent treatments at high temperatures would supply the energy required to break the water-cellulose bonds and allow the eventual aggregation of elementary fibrils along these planes. Such an increase in the lateral dimensions of already existing crystallites would not alter the L.O.D.P. but would decrease the surface-to-volume ratio of crystalline material. This should be reflected in a decreased rate of hydrolysis. The data given in Table IV agree with this hypothesis. Thus, the rate (as indicated by the slope of the regression line) decreases from 0.0305–0.0325 for untreated samples, to 0.0278–0.0292 for "pressure-boiled" yarns, and 0.0265–0.0280 for kiered material. Anomalies occur in the alcohol-extracted series, possibly because the conditions existing during this treatment were on the borderline for transition of amorphous to crystalline.

TABLE IV. Rate of Acid Hydrolysis of Crystalline Cellulose for Three Varieties of Cotton after Various Treatments as Indicated by Slope of Regression Line of Log Residue Per Cent vs. Time

Variety	Untreated	Alcohol-Extracted	"Pressure-Boiled"	Kiered
	Slope of Regression Line (−log %/hr)			
Stoneville	0.0320	0.0320	0.0292	0.0280
Deltapine	0.0325	0.0305	0.0284	0.0268
S × P	0.0305	0.0298	0.0278	0.0265

Sorption of moisture by cotton is a function of available internal surface and probably also of the nature of that surface. Internal surface, although related to crystallinity, is not necessarily correlated with it to a high degree; that is, a sample might be of high crystallinity yet because of previous sample history might have a relatively large surface available for sorption. For instance, Forziati and coworkers [3] have shown that soaking in water at room temperature, soaking with agitation at room temperature, and boiling in water will successively increase the surface of cotton fibers available for nitrogen sorption after the water is removed by solvent exchange. Likewise, the nature of the sorbing surface can make a difference. Alcohol removes the 0.6% of wax normally occurring on cotton fibers. This wax is water-repellent; therefore, its removal would increase the sorptive capacity of whatever proportion of the surface it previously occupied.

Moisture-regain data for the variously treated samples of this study are given in Table V and are plotted against per cent crystallinity in Figure 1. The precision of the moisture-regain values was computed to be better than 1%.

A statistical analysis of variance of the moisture-regain data showed that two of the main sources of variance, "treatment" and "relative humidity," and two of the interactions, "treatment × relative humidity" and "treatment × variety," were significant at $P < 0.01$. "Variety" and the interaction, "relative humidity × variety," were not significant even at

TABLE V. Moisture-Regain Data on 3 Varieties of Cotton before and after Treatment

Treatment and Variety	Moisture Regain at 11% R.H. (%)	23% R.H. (%)	33% R.H. (%)	44% R.H. (%)
Untreated				
Stoneville	2.70	3.89	4.66	5.48
Deltapine	2.60	3.75	4.50	5.35
S × P	2.70	3.82	4.62	5.42
Alcohol-Extracted				
Stoneville	2.74	3.98	4.74	5.60
Deltapine	2.74	3.92	4.76	5.60
S × P	2.77	4.04	4.86	5.68
"Pressure-Boiled"				
Stoneville	2.59	3.77	4.62	5.48
Deltapine	2.56	3.78	4.54	5.38
S × P	2.71	3.81	4.68	5.51
Kiered				
Stoneville	2.36	3.50	4.22	5.02
Deltapine	2.41	3.58	4.36	5.09
S × P	2.36	3.52	4.28	5.02

$P = 0.05$. The significant role of changes in relative humidity in affecting regain is well known and need not be discussed. That the various treatments made significant differences in regain is additional evidence that the treatments produced changes in internal structure. The magnitude of the effect of treatment on regain is, however, not large. For instance, at 44% R.H., the kiered yarns averaged 5.05% moisture; the untreated, 5.42%; the "pressure-boiled," 5.46%; and the alcohol-extracted, 5.62%. The significant interaction, "treatment × relative humidity," may be interpreted as indicating that the regain after the various treatments did not increase in the same proportion at increasing relative humidities. This is reflected in the internal surface-area calculations, which will be discussed later. The significant interaction, "treatment × variety," apparently indicates that there was a differential response of the 3 varieties to the various treatments insofar as the physical property of moisture regain is concerned, even though there are no significant differences between varieties when all treatments are lumped together. The nonsignificance of "variety" is of interest because the S × P cotton was consistently lower in crystallinity, yet failed to have consistently higher regain. This is in agreement with preceding remarks to the effect that crystallinity and regain are not necessarily closely correlated.

When the relation between acid-hydrolysis crystallinity and moisture regain is examined (see Figure 1), it is seen that there is a trend of decreasing regain with increasing crystallinity, amounting to about 0.2% per 10% crystalline; however, the correlation is only moderate. For instance, at 11% R.H. the coefficient of linear correlation of regain with crystallinity is $r = -0.494$.

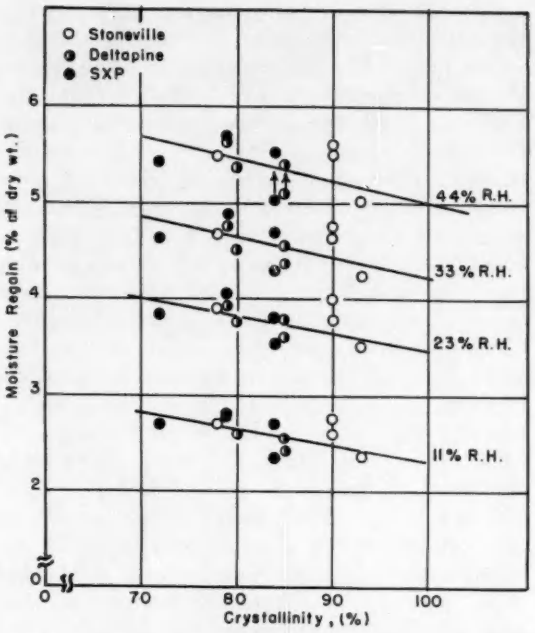

Fig. 1. Relationship between moisture regain and crystallinity.

The relations between internal surface, crystallinity, and hydrolysis rates are of interest. The surface areas, calculated from moisture-regain data by the BET equation, are given in Table VI. As might be expected, they follow the same pattern as the regain data but perhaps emphasize the greater surface available for moisture sorption after alcohol extraction and the decrease in surface after kiering. The correlation between crystallinity and surface area is

TABLE VI. Internal Surface Areas of 3 Varieties of Cotton before and after Various Treatments, as Calculated from Moisture-Regain Data by the BET Equation

Variety	Surface Area after Treatment: Untreated (sq m/g)	Alcohol-Extracted (sq m/g)	"Pressure-Boiled" (sq m/g)	Kiered (sq m/g)
Stoneville	116.1	118.7	117.5	107.6
Deltapine	113.6	118.6	114.9	109.4
S × P	113.6	120.9	117.1	108.0

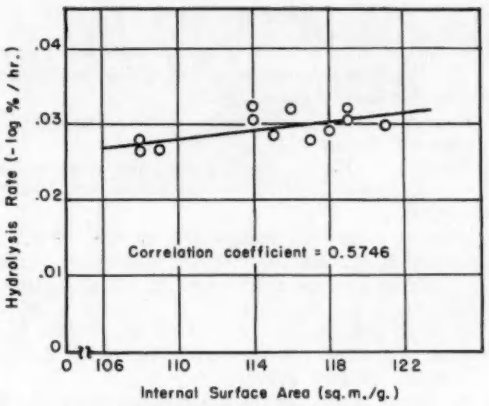

Fig. 2. Relationship of hydrolysis rate to internal surface area.

low (correlation coefficient, $r = -0.234$). The correlation of hydrolysis rate with surface area is somewhat higher ($r = 0.575$) but still is not very good. The data are plotted in Figure 2.

Even though the positive correlation of rate with surface is not very great, it is in line with the hypothesis that acid hydrolysis occurs at the surface of cellulose crystalline areas. The amorphous areas, considered to be entirely "surface," are fast reacting; hydrolysis-rate data were not obtained on the amorphous fractions in this study, since hydrolytic dissolution was allowed to proceed until essentially all of this fast-reacting material had been removed before weight-loss measurements were made. The crystalline areas are believed to be attacked only on the outside of the crystallites; hence the rate of hydrolysis of the crystalline portion (as shown in Table IV) is governed by the ratio between surface and volume.

From the evidence presented, it seems justifiable to conclude that kiering and "pressure boiling" permit crystallization of some amorphous cellulose in raw cottons, and that alcohol extraction may also do the same to some extent.

Evidence from other studies on the effect of heat plus moisture on crystallization of cellulose is not directly applicable to cotton since most of these studies were made on rayons, cellophane, or cellulose derivatives. It does, however, illustrate the combined effects of heat and water. For instance, Waller, Bass, and Roseveare [20] studied rayon tire yarns and suggested that heating in the presence of moisture and air resulted in an increased crystallinity. Ingersoll [8] had previously presented X-ray data showing marked recrystaliization of rayon on heating for 24 hr at 150°C in the presence of air and moisture; he ascribed this to mild chemical degradation which allowed the chains to reorient. Pinte, Pierret, and Rochas [14] studied changes taking place in viscose and acetate rayons as a result of steaming and proposed, as an explanation for the apparently anomalous results (decreased swelling and rate of dyeing accompanied by increased rate of moisture regain), the formation of more hydrogen bonds in the semiorganized regions (essentially an increase or improvement in crystallization) and at the same time an opening up, or greater porosity, of the amorphous regions. Preston, Nimkar, and Gundavda [15] reported that steaming produced decreased swelling, moisture absorption, and dye absorption and increased the density of rayons (viscose and cuprammonium) and silk. Simril and Smith [17] found that exposure of cellophane to high humidities at as low a temperature as 50°C modified the subsequent sorptive capacity. Howsmon [7], on the other hand, showed that treatment of rayon yarns with water at 50°C did not cause any appreciable change in X-ray pattern or moisture regain.

All of these authors were working with regenerated cellulose or cellulose derivatives which would be in a metastable state with respect to submicroscopic fine structure and hence would be expected to undergo changes rather easily. The molecular organization of the cellulose in the cotton fiber, however, has been thought to be fairly well stabilized once the fiber has lost its original swollen condition during the ripening of the boll and therefore should be relatively insensitive to such comparatively mild treatments as heating in water or dilute aqueous solutions.

The previously mentioned work by Nelson and Conrad [10] on the effects of various purification treatments on the crystallinity of 1 normal cotton and 2 very immature cottons did not produce evidence conclusively indicating an increase in crystallinity, partly because of the magnitude of the standard errors of the crystallinity values and partly due to the few samples examined. In view of the results of the present experiments, the data of Nelson and Conrad (see Table VII) should be reconsidered. No change would be expected in the crystallinity of cotton linters, nor was any found, since this material had already been subjected to commercial kiering

TABLE VII. Degree of Crystallinity of Different Cotton Samples before and after Certain Purification Treatments *

Material	Not Extracted	Hot Alcohol Extraction Followed by Extraction With: Water (Control)	NaOH	Ethanolamine
Cotton linters	0.88	—	0.89	0.89
Normal cotton	0.84	0.84	0.86	0.86
Immature cotton	0.81	0.86	0.86	0.87
Green lint cotton	0.81	0.81	0.83	0.86

* From Nelson and Conrad [10].

and bleaching operations. The normal cotton showed only a 2% change, which was not originally considered significant; the very immature cotton showed an appreciable increase after each of the purification treatments, while the green lint cotton showed a considerable increase only after ethanolamine treatment, which takes place at a high temperature (about 169°C). These increases in crystallinity should now probably be considered significant in light of the present study.

Conclusions

From the data here presented it is concluded (1) that standard purification treatments can increase the crystallinity of raw cotton cellulose; (2) that the extent of this increase varies considerably with the individual sample; and (3) that the crystallinity values which have been reported in the literature for purified cottons are probably higher than those of the native cottons because of changes in crystallinity induced by the purification treatments.

Acknowledgments

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A Useful Cross-Sectioning Slide and Some of Its Applications

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THIS LABORATORY has for some time employed a cross-sectioning slide for textile fibers and yarns which has a number of particularly useful applications.

Description of the Slide

The slide is 1 × 3 × 0.015 in. and is made from matte-surfaced black Plastocel,[1] a carbon-impregnated acetate plastic. It is perforated with 3 parallel rows of 12 holes each, the holes being 0.035 in. in diameter and spaced ¼ in. apart. The center row is centered in the slide, the outside rows being therefore ¼ in. above and below this row. The slides are cut and perforated by a special die and punch developed at American Enka Corporation.

Although similar in general principle, the slide is a considerable improvement over a much heavier brass slide which has been in use in the United States and abroad.

These advantages lie (*a*) in its comparative thinness; (*b*) in the resiliency of the plastic, which allows more compact filling of the holes, thus preventing falling out of cut sections; and (*c*) its black matte surface, which allows pencil labeling on the slide.

Sample Preparation and the Method of Sectioning

Multiple Strands

The necessary apparatus—slide, needle threader, razor blade, scissors, and sample and filler thread—is illustrated in Figure 1*a*.

The preparation of a sample is simple: A bundle of filaments is pulled through one of the holes with a needle threader. It is then pulled carefully backward and forward slightly with the fingers, to parallel or align the filaments. The bundle is then cut close to the surface of each side of the slide.

In any case the hole must be filled snugly. Where the sample itself is too small, it may be supplemented with black-dyed viscose rayon fibers or with yarns of dissimilar cross-section character or color. Rayon, nylon, cotton, and wool have been used for this purpose.

It should be noticed that pulling the thread through the hole with the needle threader doubles the thickness of the bundle. This must be considered in selection of the quantity of sample and filler yarn used.

After preparation the slide is fastened to a glass 1 × 3-in. microscope slide with Scotch tape, and the sections are covered with a dry glass cover slip before examination. This lessens the surface glare.

Bright or semidulled yarns may be examined immediately under the microscope. Pigment-dulled rayons and other yarns that are not sharply clear may be mounted in a suitable liquid. This must not cause discoloration, should result in minimum swelling, and should be of a refractive index considerably higher or lower than that of the sample. One of the Shillaber liquids[2] of 1.660 n_D has been found very satisfactory.

In addition good results may be obtained with a mountant made from a 50-50 glycerin-India ink mixture, which is allowed to penetrate between the cut filaments or which may be wiped over the cut filament sections or applied to the thread as a size before section preparation.

In each instance excess is blotted from the surface of the treated cross sections.

Herzog also gives a method of mounting which this Laboratory finds suitable [1]. One side of the prepared and cut section is covered with a thin film of nitrocollodion. When this is dry the cut sections are next impregnated from the other side, with a suitable nonswelling mounting liquid; this displaces the occluded air between filament sections. This side of the preparation is then covered with a glass

[1] E. I. du Pont de Nemours & Co., Inc.

[2] R. P. Cargille, New York.

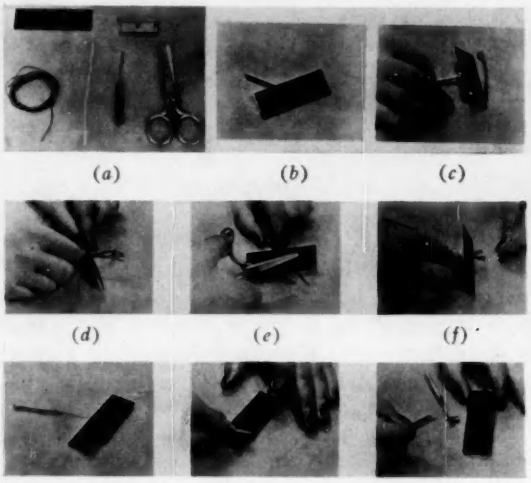


Fig. 1. *a*, Apparatus, black filler thread, and white sample thread. *b*, Use of needle threader. *c*, Introduction of black filler thread. *d*, Drawing through of black filler thread. *e*, Cutting off black filler thread to leave tuft. *f*, Introduction of single sample thread. *g*, Drawing through filler and sample thread. *h*, Cutting off thread at slide surfaces. *j*, Prepared sections in slide hole.

cover slip, and the sections may be examined or photographed.

Single Strands

To prepare a single strand, either of thread or a single filament, a slide hole is filled approximately by drawing through a bundle of filler thread. With undyed samples this Laboratory uses 150/40 viscose rayon, dyed black; for dyed samples, a filler thread of contrasting color or cross-section character is used (Figures 1*b*, *c*, *d*).

This bundle is then cut on the side opposite the needle threader to leave an open 1-in. tuft (Figure 1*e*).

The single strand is then introduced end first into the center of the tuft (Figure 1*f*), and the combination is drawn into the slide hole (Figure 1*g*). The preparation is next cut flush with the surface on each side of the slide (Figure 1*h*). Examination will then show a section of the sample in the center of the preparation (Figure 1*i*).

Applications

Fiber Identification

This method of cross-section examination allows quick identification of a fiber whenever the cross-section shape is of a significant character.

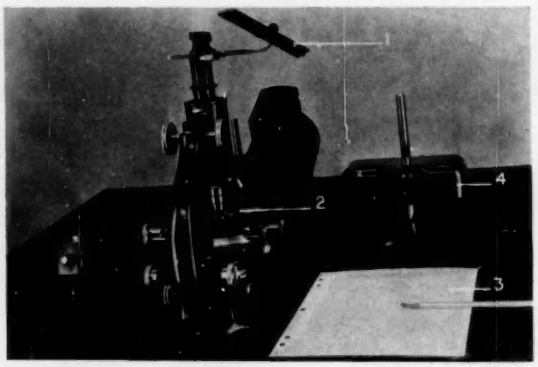


Fig. 2. Camera lucida arrangement for projection drawing. 1, Camera lucida attachment (*American Optical Co.*). 2, Section slide on microscope stage. 3, Projection drawing on graph paper. 4, Fluorescent-type lamp, used to illuminate graph paper.

In this manner many textile fibers may be easily recognized, and, in the instance of rayons, quite often distinguished as to manufacturer.

Filament Number and Denier

Similarly, particularly in the examination of rayons, filament number and approximate denier may be quickly estimated.

Filament number. For this purpose the following method is useful:

Single-thread sections of the thread or fiber to be examined are prepared as described above, placed in position on the microscope, and examined for clearness and sharpness of the cut sections, using a magnification of approximately ×150.

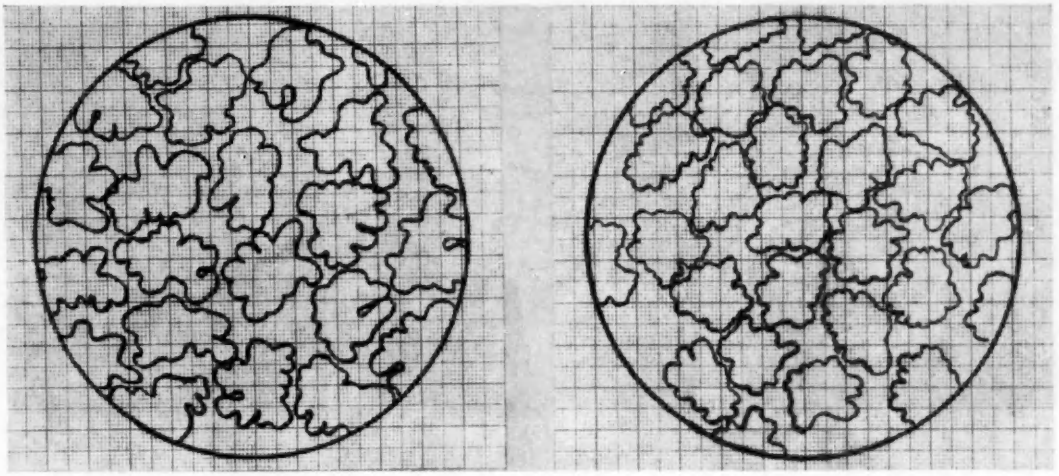
A camera lucida attachment is then affixed to the monocular tube microscope, and the image of the thread sections is projected on graph paper ruled in square millimeters (Figure 2).

Where it is desired merely to determine the filament number, filaments may then be counted, checking off the individual section images with pencil and using a hand counter.

Denier estimation. Denier is determined from the measurement of the cross-section surface, as projected and drawn on graph paper.

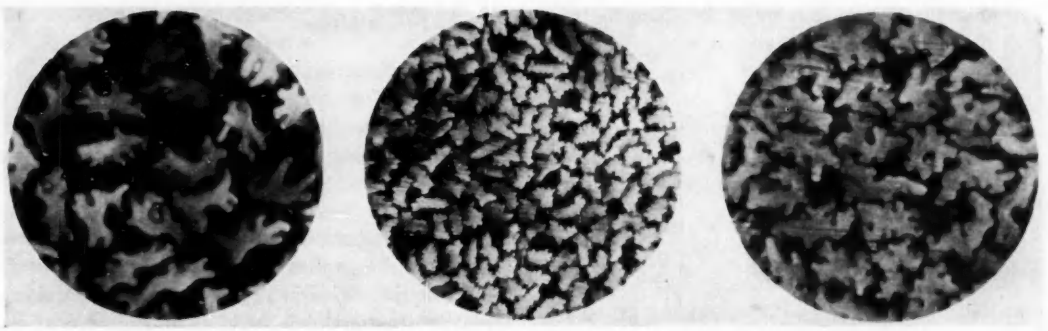
To make this estimate it is first necessary to make a calibration of the graph paper at the magnification used. This may be done in two ways.

1. Single-thread sections of two known filament/denier samples of viscose rayon, e.g., 150/40 and 100/40, are projected at a standard magnification, and drawn on millimeter graph paper, using the



(a) (b)

Fig. 3. Projection with camera lucida for denier estimation. *a*, 100/40 bright viscose rayon; *b*, 150/40 bright viscose rayon. × 750.



(a) (b) (c)

Fig. 4. *a*, Viscose rayon mounted after Herzog's method. *b*, *c*, Viscose rayon, unmounted.

camera lucida (Figure 3). Millimeter squares enclosed by the section outlines are then counted in at least 10 filaments of each preparation, and the average number per filament determined. This, divided by the theoretical filament denier, furnishes the number of squares equivalent to 1 den. Thereafter one is able to determine the denier of any single-filament cross section of viscose rayon by tracing its outline at the standard magnification used, determining the surface in square millimeters, and then dividing this figure by the equivalent of 1 den.

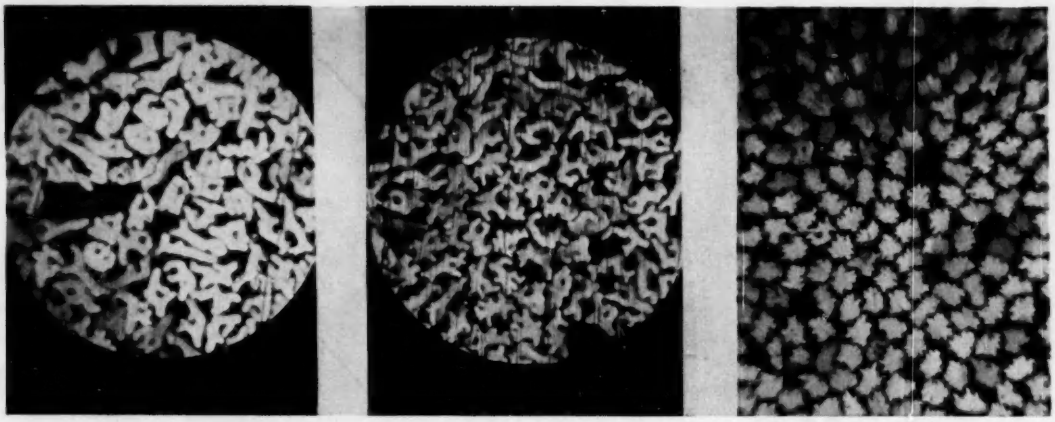
2. After projection and drawing or tracing the outline of the cross section on millimeter paper, the surface in square millimeters may be estimated with a roll planimeter or by the counting of squares, and this figure referred to Herzog's table of denier-area equivalents, calculated on the basis of surface area-specific gravity relationship [2].

In this manner the denier equivalents of such synthetic fibers as Orlon,[3] nylon, Dacron,[4], etc., may be determined in terms of viscose rayon by substituting the specific gravity value of the material involved.

Photomicrography

This method of preparation lends itself efficiently also to photomicrography. While the paraffin method of preparation and sectioning is to be preferred where great detail is desired microscopically, and subsequent study of the cross section is to be

[3] Du Pont's acrylic fiber.
[4] Du Pont's polyester fiber.



(*a*) (*b*) (*c*)

Fig. 5. Viscose rayon, dry mount, Polaroid camera photomicrographs.

made, the so-called "quick section" by means of the slide described is very acceptable where speed is essential, and little detail is sufficient.

For this purpose various mountants may be used on the prepared sections, depending upon the nature of the sample. The method of Herzog previously outlined is particularly applicable for this purpose. However, acceptable photomicrographs for record as to cross-section shape and uniformity may be made on the dry unmounted sections of "bright" yarns (Figures 4*a, b, c*).

Speed is accentuated by the use of the Land Polaroid camera, which has the advantage of producing finished prints in a very short time after the photograph is made (Figure 5).

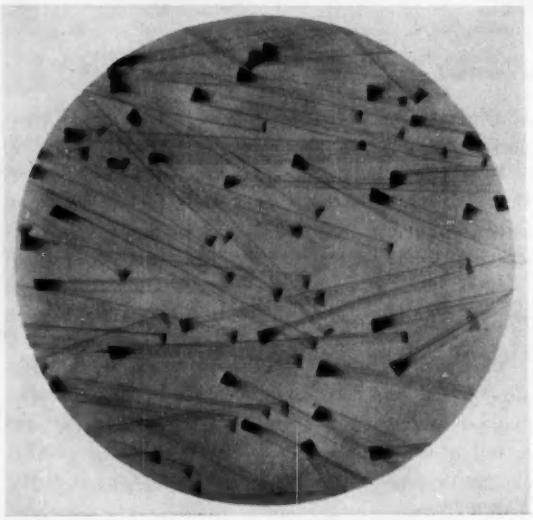


Fig. 6. Anisotropic diffusion of dyestuff [4].

Special Investigations

While the sectioning slide is relatively thin it is still useful for comparatively thick cross-section preparations as used and described recently by Iwanow and Meybeck in their study of viscose fibers [4].

A bundle of the thread or fibers to be sectioned is dipped in hot paraffin until thoroughly impregnated and is then drawn through the slide while the paraffin is still liquid. This is then cut off on each side of the slide, leaving a 1-in. tuft. The slide preparation is placed in molten paraffin for 5 min, then removed and hung up by one end until the paraffin has set. It is then further cooled in ice water until the paraffin hardens. The paraffin-impregnated yarn tufts are next cut close to the slide surfaces with a sharp razor blade.

The slide may then be immersed in a suitable dye bath for staining, the paraffin protecting all of the filaments except the sectioned ends, in this manner fulfilling the requirements for dye absorption only from the ends of the filaments.

After staining, the preparation may be washed if desired and then the plug of treated filament lengths pushed out of the slide, placed on a glass slide, and the paraffin removed by warming slightly and washing with xylol or benzene (Figure 6).

Many other useful adaptations of this slide have been made, among which, it is of interest to note, is

that of a teaching aid in textile schools. It is a matter of some satisfaction to the author that the School of Textiles of Clemson College in particular has found it beneficial [3].

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The Reaction of Formaldehyde with Cellulose

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Introduction

The reaction between cellulose and formaldehyde, originally patented by Eschalier in 1906, has received considerable attention from time to time because of the useful effects it can produce on the physical and mechanical properties of cellulosic fibers. The chemistry of the reaction has been studied by a number of workers. The work before 1942 is reviewed by Schaeffer [6], while Gruntfest and Gagliardi [2] have more recently examined the problem. The author has made some observations in the rock salt region of the infrared spectrum which he believes may contribute to understanding this reaction.

Procedure

Films of cellulose from 2.5 to 5.0 μ thick were prepared by deacetylating films of cellulose acetate which had been cast from acetone solution on mercury [5]. The spectra were obtained with a Perkin-Elmer Model 12-C recording infrared spectrophotometer by a technique which has been previously described [7]. The films were treated with formaldehyde after being mounted on the brass frames which hold them in the desiccated spectrophotometer cell. The frame and sample were dipped into an aqueous solution of catalyst, usually boric acid, and dried. Then the mounted sample was sealed in a Pyrex glass tube with 1 g of paraformaldehyde and heated in an oven at 120°C for 24 to 48 hr [8]. A number of samples were treated in tubes where a very small pinhole was left in the seal so that the vaporizing formaldehyde would sweep out any water produced in the reaction, and thus make it go further toward completion. However, whether the tube was completely sealed or not made no difference in the results.

When the samples were taken from the sealed tubes, they were washed for several hours in many changes of distilled water and desiccated for 18 hr in vacuo over magnesium perchlorate before the spectra were obtained. The spectrum of each cellulose film was also obtained before treatment to make sure that deacetylation was complete and to compare with its spectrum after treatment.

Results

The spectra of a cellulose film before treatment and after 24 hr of reaction are shown in Figure 1. The film was 3.2 μ thick, and saturated boric acid was used as a catalyst. The reaction caused the absorption band at 2.92 μ to be reduced, and that at 3.43 μ to be slightly increased. A sharp strong absorption was produced at 5.72 μ, and the heavy absorption from 8.5 to 11 μ was enhanced, particularly in the 10–11-μ region, so that the sharp cellulose band at 11 μ appears only as a shoulder of a very large absorption band.

Samples treated exactly as above except that the paraformaldehyde was omitted did not change in

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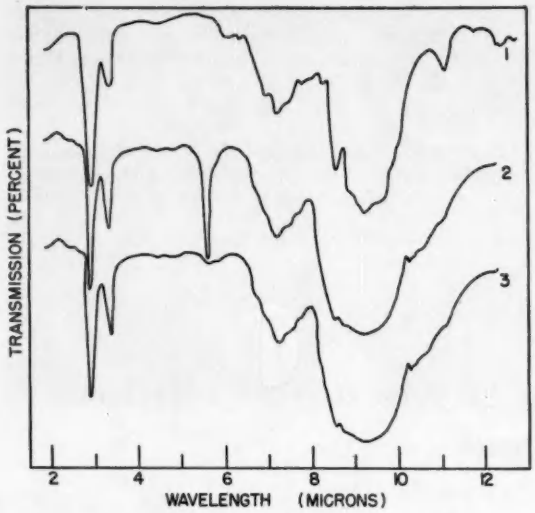

Fig. 1. The effect of formaldehyde on the infrared spectrum of cellulose. 1, Spectrum of a cellulose film 3.2 μ thick; 2, spectrum of the same film after treatment with gaseous formaldehyde in the presence of an acid catalyst; 3, spectrum of treated film after being washed in boiling distilled water for 30 min.

infrared absorption. Similarly, no change in spectrum was observed when the catalyst was omitted. The presence of boric acid in the catalyzed film could not be detected spectroscopically. Diammonium phosphate as a catalyst gave the same results as boric acid.

When the treated film was washed in boiling distilled water, the sharp band at 5.72 μ disappeared after 15 to 30 min of washing, as shown in spectrum 3 of Figure 1. The other absorption bands were not perceptibly changed. However, treatment with boiling 0.1 *N* hydrochloric acid reversed the spectral changes caused by the reaction and in 30 to 45 min completely restored the original spectrum of the film.

Discussion

The probable processes involved in the treatment of cellulose with formaldehyde are usually considered to be:

1. Formation of cellulose hydroxymethyl ether:

$$\text{Cel—O—CH}_2\text{—OH}$$

2. Formation of hydroxypolyoxymethylene cellulose ethers:

$$\text{Cel—(OCH}_2)_n\text{—OH}$$

3. Formation of methylene ether crosslinks:

$$\text{Cel—O—CH}_2\text{—O—Cel}$$

4. Formation of polyoxymethylene ether crosslinks:

$$\text{Cel—(OCH}_2)_n\text{—O—Cel}$$

5. Deposition of formaldehyde polymers in or on the cellulose.

The spectroscopic evidence obtained in this work has been interpreted as indicating that process 3 occurs predominantly in the acid-catalyzed reaction of cellulose and formaldehye.

Figure 2 shows the 3-μ region of the cellulose spectrum before and after treatment. The absorbance (optical density) was determined by the baseline method. Only processes 3 and 4 would cause a reduction in the number of hydroxyl groups and a decrease in the absorption at 2.92 μ attributed to their stretching vibration. The observed decrease must be due to the formation of crosslinking ether bridges. Although the exact amount of formaldehyde in these films is unknown, samples of cotton cellulose treated under the same conditions contain

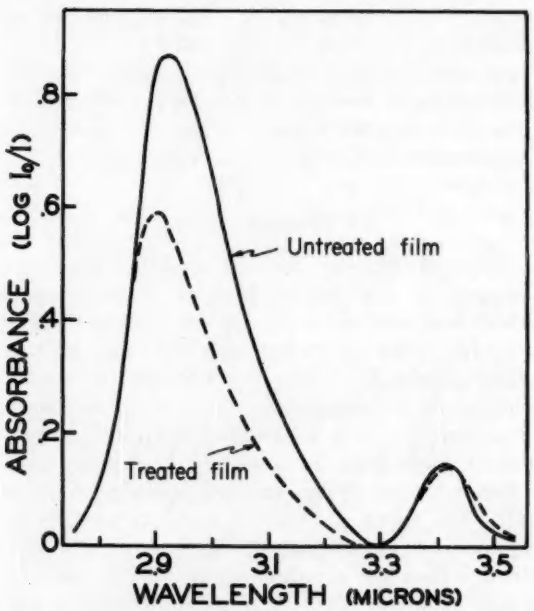

Fig. 2. Absorbance of a cellulose film in the 3-μ region before and after treatment with formaldehyde.

4 to 5% of formaldehyde [8]. If 4.5% formaldehyde was reacted in such a way that each molecule was bound to 2 cellulosic hydroxyl groups (process 3), about 0.17 of the total number of hydroxyls would be involved.

The film whose spectra are shown in Figure 2 was 4.6 μ thick and was treated with formaldehyde for 24 hr, using boric acid as a catalyst. The reduction in the intensity of the O—H band is very unsymmetrical. The integrated absorption [2] at various stages of treatment for this band and for the C—H band at 3.43 μ was measured, and the results are given in arbitrary units below:

	A_{CH}	A_{OH}
Original film	1.3	14.6
After formaldehyde treatment	1.4	11.1
After 30 min boiling in water	1.4	10.8
After 30 min boiling in 0.1 *N* HCl	1.3	13.3

The hydroxyl-band absorption of the reacted film, about 11 arbitrary units, was compared with the hydroxyl absorption of cellulose films of varying thickness, as shown in Figure 3. The absorption of the reacted film is approximately that of an untreated film 3.4 μ thick. Assuming that there is no concentration effect, this indicates that $\frac{4.6 - 3.4}{4.6}$, or 0.26, of the hydroxyl groups have been removed by the reaction. If only process 3, the formation of methylene bridges, is occurring, so that each formaldehyde was bound to two hydroxyl groups, the loss of 0.26 of the hydroxyl groups would correspond to a formaldehyde content of 7%. This figure would be a lower limit since the reaction assumed in its calculation consumes the least formaldehyde for each hydroxyl group reacted. If any of the other suggested processes is occurring, the calculated amount of reacted formaldehyde would be increased. The calculated content of 7% is about half again as much formaldehyde as is reacted with cotton under the same conditions [8]. This greater reactivity for regenerated cellulose is, of course, to be expected. It is unfortunate that analyses could not be obtained on the films at the time this work was done. However, it does not seem likely that their actual formaldehyde content could be greater than that of cotton by a factor of more than 2 in this dry reaction system.

[2] This was determined by measuring the area bounded by the absorption curve and the base line. Absorption rather than absorbance was used so that this area determination could be done on the original spectrophotometer record.

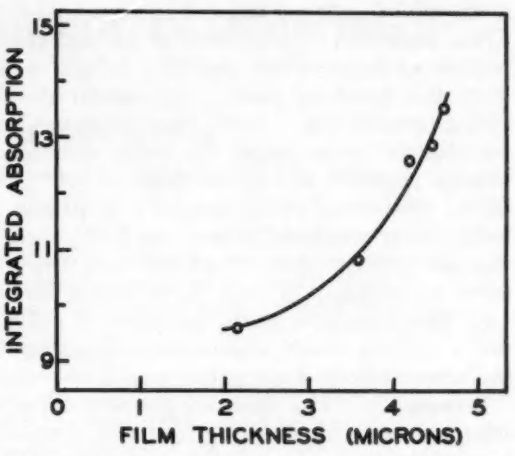

Fig. 3. Integrated absorption of the O—H group stretching vibration for cellulose films of different thickness.

Therefore, it seems reasonable to conclude that under the given conditions of reaction the most important process involved is the reaction of a single molecule of formaldehyde with 2 hydroxyl groups on adjacent cellulose chains to form a methylene bridge between them. The absorption at 3.43 μ due to C—H stretching vibrations would be expected to increase as a result of any of the processes listed above.

The band at 5.72 μ which appears upon treatment with formaldehyde is no doubt assignable to the carbonyl group, most likely the aldehydic carbonyl of formaldehyde itself. The latter has been reported at 5.71 μ [1] and at 5.73 μ [4]. For acetaldehyde, the corresponding band is at 5.75 μ [3]. Since this strong band in the treated film is removed by hot-water washing, it is to be associated with unbound formaldehyde such as might result from process 5 above. However, trioxane and paraformaldehyde, the most common polymers of formaldehyde, would not be expected to have absorption bands here, and we have confirmed that they do not, even when freshly sublimed. There is the possibility that the absorption arises from some other polymer containing free aldehyde groups, and that hot water either dissolves or hydrates it. The absence of an absorption band in freshly sublimed paraformaldehyde, as well as the failure of this material to show reducing properties, indicates that this is not likely.

It is known [2, 8] that some unbound hot-water-soluble formaldehyde is added to the cellulose under reaction conditions such as those used in this experi-

ment, and it is obvious that this material causes the 5.72 μ absorption. Since there is no well-known polymer of formaldehyde absorbing here, it seems likely that this band results from molecularly absorbed formaldehyde. The spectral absorption was not changed by prolonged evacuation over phosphorous pentoxide nor by evacuation at 120°C for 60 hr. Immersion of the film for 5 to 10 min in boiling water completely removed the 5.72-μ absorption and reduced slightly the 3.43-μ band, but produced no detectable changes in the region beyond 7 μ. The latter observation also makes it unlikely that a polymer, which would contain C—O bonds, was removed in the washing.

Between 8 and 11 μ there is a general increase in absorption after formaldehyde treatment, especially between the heavy absorption centering about 9.2 μ and the smaller cellulose band at 11.15 μ. It has not been possible to assign absorption bands in this region, but skeletal vibrations of the glucose rings and chains, as well as the various C—O bonds present, are probably the chief contributors. The broadening and strengthening of the bands in this region may be interpreted as changes in skeletal vibrations due to the addition of cross-links and/or to the introduction of new types of C—O bonds. At present there is no way of identifying these spectral changes with any one of the five processes listed above, but, since they persist after the film is washed in boiling water, process 5 can be eliminated as their source. Treatment with 0.1 *N* HCl at the boil for 30 to 45 min completely reverses the spectral changes in this region, and the original cellulose spectrum is restored.

Conclusions

From observations of the changes produced in the infrared spectrum of cellulose upon treatment with formaldehyde, it has been shown: (1) that the number of free hydroxyl groups in the product is less than in the original cellulose, so that crosslinking must have occurred; (2) that the crosslinks most frequently occurring are methylene groups rather than polyoxymethylene chains; and (3) that the unbound formaldehyde present on the cellulose after the reaction, which can be removed by hot-water washing, is either molecularly adsorbed formaldehyde or some uncommon polymer of formaldehyde containing free aldehyde groups.

Acknowledgments

Mr. E. B. Jeffries and Mrs. Helen Lyons assisted in carrying out this work. We also wish to thank the Office of Naval Research for its support of the program under which this research was done (Contracts No. NONR-09000 and NONR-09001).

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The Soiling Characteristics of Textile Fibers[1]
Part I

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Abstract

Methods are described for measuring the comparative soiling tendencies of textile fibers. It is shown that reflectance readings on soiled fibers measure an overall effect, part of which can be attributed to the weight and particle-size distribution of the retained soil, and part to the optical properties of the fibers themselves. It is suggested that the "effective soil content," which is defined as the weight of soil retained multiplied by the specific absorbance (of light) of that soil, is a more significant criterion of soiling than is either the weight of soil retained or the decrease in reflectance produced by the soil. Relative values for the effective soil content can be calculated from reflectance readings through use of the Kubelka-Munk equation. The soil retention of the fibers studied increased in the following order: cotton, acetate, viscose rayon, nylon (variable, depending on soiling conditions), wool. The same order was maintained when the time of contact with the soil varied from 5 to 80 min. The soil retention of all the fibers increased with decreasing moisture content of the yarn. The presence of even small amounts of oily material in the yarn increased substantially the amount of soil retained.

THE SOILING characteristics of textile fibers have, until recently, received comparatively little attention in the literature. While it is true that the literature on detergency contains many references to the preparation of artificially soiled fabrics, these have been concerned mostly with a single fiber type (cotton) and with methods of soil removal rather than those of soil acquisition.

In some cases conflicting views have been expressed regarding the relative soilability of various fibers. For example, Hall [8] states that cotton and wool in the form of apparel fabrics soil more readily than viscose rayon or acetate. This is confirmed, with respect to wool and viscose, by the work of Whewell, Messiha, and Selim [27], who subjected similarly constructed fabrics of wool, viscose rayon, and blends of the two fibers to indoor and outdoor exposure. They found that the wool soiled more readily than the viscose; and in blends, the higher the wool content, the heavier was the soiling. Further confirmation is provided by the work of Hart and Compton [10], who subjected fibers previously ground in a Wiley mill to soiling by aqueous dispersions of carbon blacks of varying particle size. They found that the natural fibers (wool, silk, cotton, linen) soiled more heavily than the synthetic fibers (nylon, acetate, viscose rayon), the wool being soiled most heavily of all. On the other hand, in the carpet field, it appears to be generally agreed [7, 18, 22] that most viscose rayons and acetate are more susceptible to soiling than wool, although a recent publication [22] describes a specially prepared viscose rayon for use in carpets which is claimed to be equal to or better than wool with respect to soiling properties. Masland [18] concluded that soiling is primarily a function of the diameter and cross-sectional shape of the fiber, the origin of the fiber, whether synthetic or natural, animal or vegetable, being of little consequence, except insofar as origin influences morphology.

A committee of the New York Section, AATCC, under the chairmanship of E. W. K. Schwarz [23], has reviewed the published work pertinent to fabric soiling, and the conclusions reached may be summarized briefly as follows: Dirt particles may be brought in contact with fabrics by diffusion, deposition, or interception from the air, by direct transfer from another surface, or by electrostatic attraction. Having been brought in contact, particles may adhere to fibers by mechanical forces or occlusion in irregularities in the fiber surfaces, by oil bonding, and possibly by electric forces. The mechanisms of

[1] N.R.C. Publication 3617.

impingement and of retention are separate and independent factors in soiling, with the possible exception of electrostatic forces which may both attract and hold particles to fibers. Generally speaking, retention is a function of the fibers while impingement is a function of the service or test conditions. The degree of soiling is a result of both functions.

The present work was undertaken for the purpose of determining the relative soilability of various fiber types under standardized soiling conditions. Of the three test methods suggested by the AATCC Committee [23], the blower test would seem to be too sensitive to variations in fabric construction to be useful for comparing fiber types, while the floor test is applicable primarily to floor coverings. Furthermore the quantity and possibly the type of soil to which the test specimens are subjected in both of these tests are uncontrolled variables, so that in comparing a series of fibers it would be necessary to carry out all tests simultaneously. The tumbler test, on the other hand, may be used to compare the soiling properties of a wide range of fabrics when soil impingement occurs principally by deposition and direct transfer. The soiling conditions are reproducible; hence comparative tests need not be run simultaneously. Consequently in the present work a modification of the AATCC tumbler test [23] has been employed. Since it was desired to measure the inherent soiling characteristics of the various fibers, soiling conditions were selected, insofar as possible, to eliminate or to maintain at constant values those extraneous influences which are believed to contribute to fabric soiling but which are not inherent characteristics of the fibers themselves. For example, the influences of fabric construction and of oil bonding on soil retention were eliminated by using solvent extracted yarn as the test material.

Experimental

Materials

The fibers studied were obtained in the form of unbleached carpet yarns and are listed in Table I. With the exception of the cotton, all yarns were woolen spun. Prior to testing, the yarns received the following preliminary treatment.

Cotton (*C*). The yarn was extracted for 24 hr in a Soxhlet apparatus with 1:1 (by volume) methanol-benzene. After evaporation of the solvent the yarn was immersed for ½ hr in boiling water and then rinsed thoroughly in cold water. The yarn was then immersed for ½ hr in 0.3% hydrogen peroxide solution at 85°C and *p*H 10.5, this *p*H being attained by the addition of ammonium hydroxide. After a final rinsing in cold water the yarn was air dried and conditioned at 70 ± 2°F and 65 ± 2% R.H.

TABLE I. Description of Yarns Used

Designation	Fiber Type	Equivalent Cotton Count	No. of Plies	Delustrant Content (TiO_2)%	Composition
C	Cotton	1.21	6	—	—
V_1	Viscose rayon	0.97	2	0.78	*
V_2	Viscose rayon†	1.03	2	0.70	15-den filament
A	Acetate	0.91	3	1.11	67% 17-den filament + 33% 12-den
N	Nylon	1.18	2	0	15-den filament
W_1	Wool	1.08	2	—	40's grade
W_2	Wool	1.13	2	—	46's grade
WV	Wool-viscose blend	0.83	2	0.53	55% wool, 36's grade; 45% viscose (60% 22-den + 40% 14-den)

* The exact composition is not known. Microscopic examination indicated a high percentage of low-denier filaments, probably in the range of 2–4 denier, with smaller amounts of higher-denier filaments.

† This yarn was a specially prepared carpet rayon, the filaments of which had an approximately circular cross section.

Viscose rayon (*V_1 and V_2*). The yarn was extracted for 24 hr with benzene, rinsed with water, dried, and conditioned.

Acetate (*A*). Same as viscose rayon.

Nylon (*N*). Same as viscose rayon.

Wool-Viscose (*WV*). The yarn was extracted for 6 hr with diethyl ether, air dried, extracted for 24 hr with 95% ethyl alcohol, and rinsed with water. It was then bleached by immersion for 24 hr in warm (about 45°C) 1% hydrogen peroxide solution adjusted to *p*H 8.0 with ammonium hydroxide. The yarn was then rinsed thoroughly with water, dried, and conditioned.

Wool (*W_1*). Similar to wool-viscose, except that the yarn was given a single 24-hr extraction with benzene instead of consecutive extractions with ether and alcohol.

Wool (*W_2*). Same as wool-viscose.

Distilled water was used in the fiber-purification processes.

The soil used throughout this work was obtained from vacuum-cleaner sweepings. Since this soil

TABLE II. Analysis of Soil

Ether soluble (fatty matter)	7.9%
Unsaponifiable matter (included in total fatty matter)	3.9%
Loss at 105° (moisture)	1.4%
Loss on ignition at 500°C (organic matter)	58.2%
Residue on ignition at 900°C (mineral matter)	39.1%

consisted of dirt which had accumulated by settling or deposition on carpets under service conditions, it was believed initially that it would provide a more realistic soil than would be provided by a synthetic soil prepared from carbon black or other artificial soiling agents. A similar type of soil has been used by Fortess and Kip [7], Masland [18], and others in soiling studies.

However, it cannot be expected that the data obtained will correlate with soiling under service conditions, since they are based on a single and arbitrary set of soiling conditions with only one type of soil, and with the elimination of at least some of the factors that normally contribute to fabric soiling. Moreover, as the work progressed, it became obvious that the choice of a heterogeneous soil tended to complicate the theoretical treatment of the data. Nevertheless it is believed that the data obtained are of interest since they throw some light on the mechanism of the apparent soilability of the various fibers studied.

The crude material was first heated at 130°C for about 60 hr to sterilize it, and it was then screened, the portion passing an 80-mesh screen being retained. A sufficient quantity of soil for all the tests reported was prepared at one time, so that the quality of the soil used was constant throughout. The soil was dark brown in color, and microscopic examination showed the presence of a considerable number of broken fragments of wool fibers. An analysis of the material is given in Table II. The soil was conditioned at 70 ± 2°F and 65 ± 2% R.H. prior to use.

Method

The conditioned yarn was cut into 6-in. lengths, and a 3-g sample was transferred to a 1-pint glass Launder-Ometer jar, along with the required weight of soil (5, 10, 15, or 20% of the yarn weight) and twenty ¼-in. steel balls. The jar was rotated in the Launder-Ometer at 42 rpm at room temperature for 10 min, or as otherwise noted. The soiled yarns were then removed from the jar, and one end of each length was fastened to a strip of cellulose adhesive tape, which was then folded lengthwise back over the ends of the yarns to hold them securely in place. The strip of tape was then supported in front of an electric fan and the yarns were blown vigorously for 5 min, the stream of air being sufficient to cause considerable flexing of the yarns. After blowing, the yarns were put through a mechanical chopping machine, similar to that described by Derrett-Smith and Keig [4], which cut them into lengths of approximately 1 mm and resulted in the yarns being broken up into individual fibers. This chopped-fiber technique, which leads to a more uniform distribution of the soil, was first employed by Powney and Feuell [20] and later by Compton and Hart [2]. The fibers were thoroughly mixed, were made into a flat rectangular pad of sufficient thickness to eliminate background interference, and were covered with a lantern slide cover glass. Reflectance readings were made through the glass plate with a Photovolt Model 610 reflectometer, using the green tristimulus filter. A similar cover glass was placed over the reference standard in calibrating the instrument. Readings were taken at three locations on the surface of the pad; the fibers were then thoroughly mixed, flattened, and three more readings were taken. This process was repeated once more, making nine readings in all, which were averaged to give the mean reflectance of the mass of fibers. Four such tests were carried out and the results averaged. In general the deviation from the average value was not more than 1 or 2 reflectance units.

Criteria of Soiling

Measurements of reflectance with the green tristimulus filter correspond to "luminous apparent reflectance" [12], i.e., to the grading which an average observer would assign to the surface if called upon to compare it with a scale of grays ranging between black and white. The decrease in reflectance of textile fibers resulting from the pickup of soil therefore is a measure of the visual apparent degree of soiling, and this is a very useful concept for many practical purposes. The reflectance, however, does not bear a linear relationship to the weight of soil retained by the fibers [15], i.e., the decrease in reflectance produced by the addition of soil to fiber depends not only on the amount of soil added but also on the initial reflectance of the fibers prior to the addition. Furthermore, the decrease in reflectance

measures an overall effect, some of which is due to the physical characteristics of the fibers, some to the characteristics of the soil, and some to the interaction between soil and fiber, i.e., to the weight and particle-size distribution of the soil retained by the fibers. In the following work an attempt has been made to segregate these factors and to evaluate each one separately.

For the purpose of converting reflectance readings into relative weight units a number of workers [1, 6, 16, 19, 25] have employed the Kubelka-Munk equation [14], $K/S = (1 - R)^2/2R$, in which K is the coefficient of light absorption, S is the scattering coefficient, and R is the reflectance. It has been assumed that K increases proportionately with the amount of light-absorbing material, while S remains essentially constant, so that K/S is a linear function of the weight of light-absorbing material present.

Hart and Compton [11] have given an excellent analysis of the limitations of this formula as applied to the measurement of the soil content of textile materials. They concluded that when reflectance measurements are made on thoroughly mixed, chopped fibers, so that uniform distribution and random orientation of the soil are obtained, the assumption that K is proportional to the weight of soil is valid provided that the specific absorbance of the soil remains constant. They derived the equation, $K - K' = kN\alpha G$,[2] in which K and K' are the coefficients of light absorption of the soiled and unsoiled fibers respectively, k is the coefficient of light absorption of the soiling material, N is the number of particles per gram of soil, α is the average projection area per particle, and G is the weight in grams of soil added. The term $kN\alpha$ defines the specific absorbance, X, of the soil, so that

$$K - K' = XG$$

Dividing through by S, which is assumed to be constant,[3]

$$\frac{K}{S} - \frac{K'}{S} = \frac{X}{S} G$$

Assuming for the moment that X remains constant throughout the soiling procedure, it would be possible to calculate from reflectance readings the relative weight of soil retained by the fiber for various soiling treatments. This procedure is not valid, however, for comparing the relative soil contents of different fibers, since the proportionality constant contains the term S, which is a characteristic of the fiber and may be expected to vary with different fibers.

No satisfactory method was found for evaluating S directly, but relative values of S for the various fibers were determined as follows.

Weights of soil ranging from about 0.025 to 0.1 g were thoroughly mixed with 3 g of chopped, conditioned fiber by first tumbling for 10 min in the Launder-Ometer with twenty ¼-in. steel balls, followed by hand mixing on a sheet of paper with a spatula. The mass of fibers was then formed into a thick pad, covered with a glass plate, and a reflectance reading was taken. The fibers were then further mixed by hand and a second reading was taken.

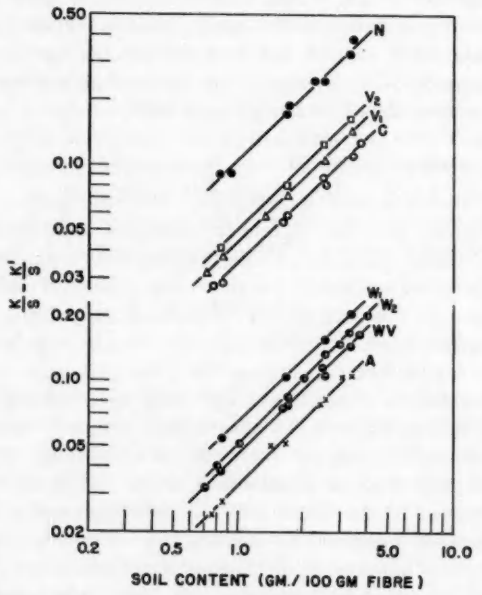

Fig. 1. Relation of $(K/S - K'/S)$ to weight of soil in soil-fiber mixtures.

[2] The terminology has been changed slightly to conform to that used throughout the balance of this paper.

[3] It is of interest to compare the equation $(K/S) - (K'/S) = (kN\alpha/S)G$ with that given by Reich, Snell, and Osipow [21], viz., $(K/S) - (K'/S) = k'G^n$, where k' and n are constants, n being a function of the particle size or degree of agglomeration of the soil. Combining the two equations and putting $N\alpha G = A$, the total projection area of the particles comprising the weight G, one gets $k'G^n = (k/S)A$, whence $n = \log (kA/k'S)/\log G$. Hence n is a function of the area of the soil particles in relation to their weight. This is essentially the significance attached to the constant n by the authors [21] and indicates that the two equations are mutually compatible.

This was repeated until a total of ten readings were obtained and these were averaged to give the mean reflectance of the mass of fibers. The maximum deviation of the individual readings from the mean was 1.8 reflectance units, and the average deviation for the whole series of readings was 0.3. The reflectance of the unsoiled chopped fiber was also determined, and the value of the expression $(K/S) - (K'/S)$ was computed and plotted, on logarithmic scales, against the soil content of the soil-fiber mixture (Figure 1), the slopes and intercepts being calculated by the method of least squares. The lines are essentially parallel, the average slope being 0.99. This indicates that for all practical purposes $(K/S) - (K'/S)$ is proportional to G. The proportionality constant X/S is given by the intercept, i.e., by the value of $(K/S) - (K'/S)$ when $G = 1$. Since X is constant in this case, the reciprocal of X/S is a measure of the relative value of S. The highest value obtained (that for the acetate fiber) was arbitrarily set at 1.00, and the values of S (rel.) for the other fibers were calculated and are given in Table III.

In the preceding discussion it was assumed that the specific absorbance of the soil, $X = kN\alpha$, was constant. Both N and α are functions of the size of the soil particle, and hence the specific absorbance can be constant only if the particle-size distribution remains constant. In the measurements of S described above every effort was made to prevent any loss of soil; hence it has been assumed that the distribution of particle sizes was, in all cases, the same as in the original soil, and therefore X was constant throughout these measurements. In the measurements of soil retention however, where the excess soil was removed by blowing, the particle-size distribution was not necessarily the same as in the original soil. It is probable that small particles are more readily retained by the fiber than are larger particles [9, 10] and therefore the specific absorbance of the soil which is retained by the fibers differs from that of the original soil, and may differ for each of the fibers studied.

The apparent soiling or "dirtiness" depends not only on the weight of soil retained but also on the specific absorbance of the soil. The latter, in turn, depends on the particle-size distribution and also, in the case of a heterogeneous soil such as that used in the present work, on the distribution of particle types, i.e., it cannot be assumed that each fiber will retain the various components of the soil in the same proportions. (The results of unpublished work quoted in the AATCC report [23] indicated that different fabrics, when soiled with a heterogeneous soil, retained the various components of the soil in the same proportions as they occurred in the original soil. According to the theories of Hart and Compton [10, 11] such a result could be obtained only if the various components of the soil had similar particle-size distributions. While this may have been true for the particular soil used in the above mentioned work, the application of these findings to all heterogeneous soils does not seem warranted.) Hence, since from a practical point of view the evaluation of soiling is primarily a visual phenomenon, it is obvious that the weight of soil retained has very little significance as a criterion of soiling.

The quantity GX, which may be regarded as representing the "effective soil content" or the "blackening power" of the retained soil, is a more significant criterion of soiling, and is readily determined from reflectance readings through conversion to the corresponding K/S values, i.e.,

$$\text{(Effective soil content) } GX = [(K/S) - (K'/S)]S$$

In the following work, relative values of the effective soil content have been calculated,[4] using the values of S (rel.) given in Table III, and these have been used as an index of the soil content of the various fibers.

TABLE III. Values of the Constants S, m, and C for Various Fibers

Fiber	S (rel.)	m	C
Cotton, C	0.93	0.62	0.119
Viscose rayon, V_1	0.74	0.75	0.146
Viscose rayon, V_2	0.65	0.78	0.161
Acetate, A	1.00	0.71	0.127
Nylon, N	0.30	0.66	0.151
Wool, W_1	0.51	0.79	0.161
Wool, W_2	0.65	0.79	0.176
Wool-Viscose, WV	0.71	0.78	0.184

Soiling Level

The soiling level (L) is defined by the following equation:

$$L = \frac{\text{Weight of soil used in test}}{\text{Weight of yarn used in test}} \times 10$$

[4] A table relating K/S to R has been published by Judd [13].

The soiling level is thus a measure of the amount of soil to which the clean yarn is exposed during the soiling test. Since 3 g of yarn was used in all cases, a soiling level of 1 corresponds to 0.3 g soil.

Soiling tests were carried out on the various fibers at soiling levels of 0.5, 1.0, 1.5, and 2.0. The results are given in Figure 2, in which the effective soil content (GX) is plotted against the soiling level (L) on logarithmic scales. Although there is some scattering of the points, the best curve that can be drawn appears to be a straight line corresponding to the equation

$$\log GX = m \log L + \log C$$

The slope m and the intercept C of each of these lines were determined by the method of least squares, and are given in Table III. The constant C gives the effective soil content of the soiled fiber at a soiling level of 1. (When $L = 1$, $GX = C$.) For those curves that are nearly parallel to each other C may be considered to represent approximately the relative soilability of the various fibers over the range of soiling levels studied. However, in comparing curves that are not parallel to each other, i.e., where the values of m differ significantly, the relative soilability depends on the soiling level at which the comparison is made. With the exception of the curves for nylon and cotton the lines are approximately parallel. No particular significance can be attached to the slope of the nylon curve owing to the extreme scatter of the experimental points for this fiber, but it would appear that the slope of the cotton curve differs significantly from those of the other fibers. The values of m and C thus define the soilability of the various fibers with respect to effective soil content.

In addition to the above considerations, the apparent visual degree of soiling produced by a given soil content is influenced by the optical properties of the fibers themselves, i.e., by the scattering coefficient S. This is best illustrated by a numerical example. Consider two fibers, A and B, each having an initial reflectance of 80% and therefore an initial K/S value of 0.025. Suppose that fiber A has a higher scattering coefficient than fiber B, owing, for example, to a higher content of delustrant. Let $S_A = 0.4$ and $S_B = 0.1$; then, since $K/S = 0.025$ for both fibers, $K_A = 0.01$ and $K_B = 0.0025$. The higher absorption coefficient attributed to fiber A might be due to the presence of a dye or other light-absorbing material. Now suppose that both fibers pick up the same amount of soil (the two lots of soil are assumed to be identical with respect to both weight and specific absorbance) and that this soil is sufficient to increase the value of K by 0.2 in each case. It follows that the values of K_A and K_B for the soiled fibers will be 0.21 and 0.2025, respectively, whence $(K/S)_A = 0.21/0.4 = 0.525$, and $(K/S)_B = 0.2025/0.1 = 2.025$. The corresponding reflectances of the soiled fibers, R_A and R_B, are then 37.4 and 17.0%, respectively; i.e., although both fibers had the same initial reflectance, and both received the same amount of soil, fiber A appears to be less heavily soiled than fiber B. In general, other things being equal, the higher the

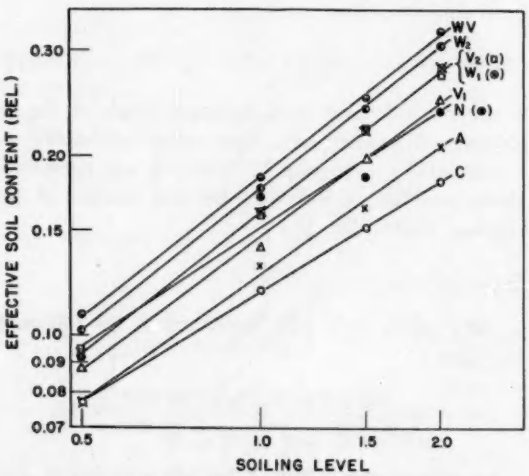

Fig. 2. Relative soil retention of various fibers.

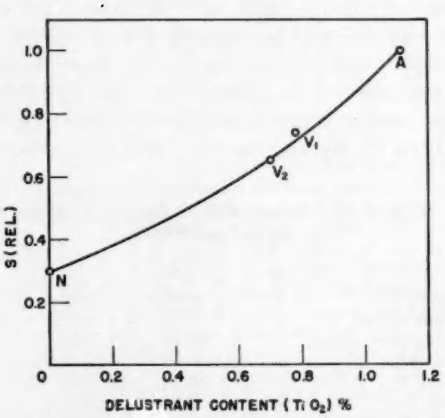

Fig. 3. Effect of delustrant content on S.

scattering coefficient of the fiber, the lower will be its apparent soilability as judged visually.

The scattering coefficient of synthetic fibers can be controlled to some extent by the addition of a delustering pigment. The influence of delustrant (TiO_2) content on S for the synthetic fibers included in this study is shown in Figure 3.

Referring to Figure 2, the fibers may be arranged in order of increasing soilability as follows: cotton, acetate, viscose, nylon (variable, depending on the soiling level), wool. This is in fair agreement with data given by the AATCC Committee [23] for the weight of soil retained by a series of pile fabrics soiled by their tumbler method, the principal point of disagreement being in the placing of the nylon fiber, which they found to be more heavily soiled than any of the other fibers.

For the sake of comparison with the curves of Figure 2, the reflectance data from which these curves were derived are given in Figure 4. As might be expected, the order of soilability based on either final reflectance or decrease in reflectance does not agree with that based on effective soil content. Nor does it agree with data given by the AATCC Committee [23] based on decrease in reflectance or with data given by Hart and Compton [10] based on final reflectance values. The two latter sets of data are likewise in complete disagreement, the AATCC data indicating that the order of increasing soilability is wool, cotton, nylon, acetate, viscose, while Hart and Compton's data indicate the order to be acetate, viscose, nylon, cotton, wool, the first three being very nearly equal. The soiling procedure and the type of soil were different in each of these three methods, and therefore some discrepancy in results is to be expected. However, the highly contradictory results obtained directly from reflectance readings, together with the somewhat better agreement found between effective soil content determined as described in the present paper and actual soil content determined by chemical analysis [23], suggests that at least some of the disagreement encountered in the former methods may be due to differences in the optical properties of the fibers rather than to differences in the amounts of soil retained.

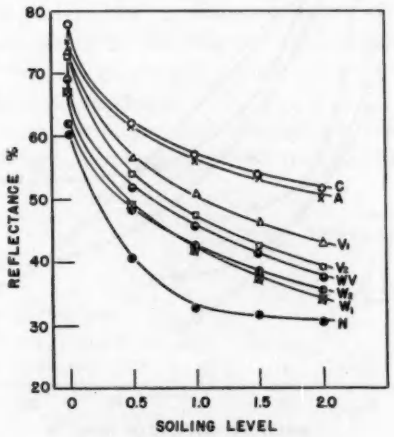

Fig. 4. Reflectance of soiled fibers.

It seemed possible that percussion with the steel balls during soiling might result in some abrasion of the fiber surface, with a resulting increase in the number of soil-holding sites. A fiber that is easily abraded would thus soil more readily than one which resists abrasion, and hence the soiling test may not measure the soilability of the fibers in their original condition. Yet the majority of methods by which dry soil may be applied to fibers or fabrics, either under actual service conditions or by an artificial laboratory test, is subject to this criticism. In any process involving the direct transfer of soil to the fiber from another surface some abrasion of the fiber is likely to occur, and even in the case of airborne soils, as for example in the soiling of flags, some abrasion may result from friction between adjacent fibers.

In the present work no change in appearance of the fibers was detected by microscopic examination at a magnification of × 500 after they had been tumbled in the Launder-Ometer for 80 min. It is probable however that some slight roughening of the surface, of submicroscopic dimensions, did occur. The extent to which such mild abrasion affects the soil retention of the fibers is not known. Compton and Hart [2] found that the retention of a coarse-particle soil by cotton was increased by repeated passes of the fiber through a Wiley mill prior to soiling, whereas the retention of a fine-particle soil was not affected. However, the amount of abrasion resulting from this treatment would be expected to be comparatively great.

In any case it would seem reasonable to classify ease of abrasion as a physical characteristic of the fiber which may possibly contribute to its soilability. Measurements of this property for various fibers,

while beyond the scope of this paper, would be of interest.

Time of Contact

In this series of tests a soiling level of 1.0 was used throughout, and the time of tumbling in the Launder-Ometer was varied from 5 to 80 min. The results are shown in Figure 5.

The amount of soil retained by the fibers increases with increasing time of contact with the soil; and even after 80 min tumbling the maximum soil holding capacity of the fiber had not been reached. The curves, with the exception of that for nylon, do not cross, so that the differences in soilability of the various fibers as established in the preceding section, while magnified somewhat with longer times of contact, are not materially altered. The curve for nylon, on the other hand, cuts across the other curves so that the soilability of this fiber relative to that of the other fibers studied depends on the time of contact with the soil. After 80 min contact the nylon fiber retained less soil than any of the other fibers and appears to have almost reached its maximum soil-holding capacity. It is probable that nylon contains fewer surface irregularities than the other fibers studied [10], and, once these soil-holding sites have become occupied, further time of contact with the soil results in only a small increase in soil retention.

Moisture Content

The influence of moisture content of the yarn on the degree of soil retention was determined. In one series of tests the yarn and soil, after weighing, were heated for about 18 hr in an oven at 105°C, cooled to room temperature in a desiccator over phosphorus pentoxide, and then soiled in the usual way. In order to determine whether or not the preliminary heating had any effect on the degree of soil retention, a few experiments were carried out in which the yarn and soil were maintained at room temperature in a desiccator over phosphorus pentoxide for several weeks prior to soiling. The results of these tests were in good agreement with those in which the yarn and soil were heated. In the second series of tests the yarn and soil, after weighing, were conditioned for several days at approximately 95% R.H. in a desiccator over sulfuric acid of sp. gr. 1.085. The soiling tests were then carried out in the usual way, the soiling level being 1.0 and the time of

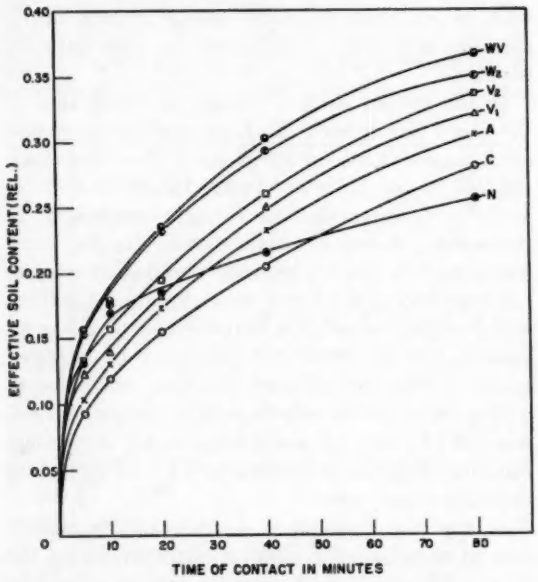

Fig. 5. Effect on soil retention of time of contact with the soil.

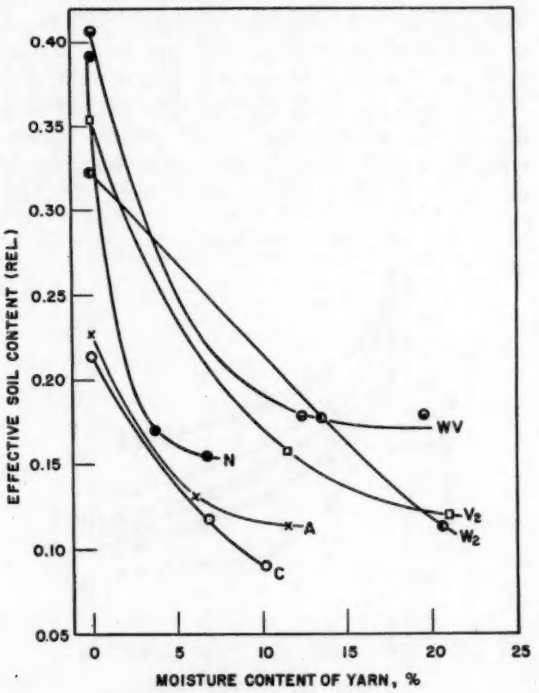

Fig. 6. Effect of moisture content of yarn on soil retention.

contact 10 min in every case. The moisture content of the yarn conditioned at 65 and 95% R.H. was determined on separate samples. The moisture content of the soil was not determined. The results are given in Figure 6.

All the yarns show increasing soil retention with decreasing moisture content. Utermohlen, Ryan, and Young [26] found that damp cotton cloth, containing about 75% moisture, was more resistant to soiling than was dry cloth when the soiling was accomplished by immersion of the cloth in dispersions of carbon black in carbon tetrachloride or water. On the other hand, moisture contents of 5 to 12%, obtained by conditioning the cloth at 35 to 85% R.H., had no influence on the degree of soiling. They concluded that the moisture present in the very damp cloth resisted displacement by the soil-dispersing liquid even when the latter was water. While this explanation does not appear to be applicable to the present data because of the different soiling technique used, it is possible that the film of moisture on fibers conditioned at high relative humidities may tend to repel the hydrophobic soil particles with a resulting decrease in soil retention.

Another possible explanation is the effect of static electrification. When textiles are processed under dry atmospheric conditions static charges are built up on the fibers, resulting in excessive soiling and many other processing difficulties [5]. Nylon, as well as some of the newer synthetic fibers, is known to be particularly susceptible to this effect, due to its low moisture absorption and low electric conductivity [17]. While all textiles are subject to static formation, the condition is largely corrected for many fibers by carrying out the processing at higher relative humidities, which results in rapid dissipation of the charge.

The test conditions used throughout this work are such as to favor a rapid buildup of static charge, i.e, the test material is electrically insulated from the surroundings by the glass container and is subjected to friction against the steel balls and the walls of the container. To what extent the influence of moisture content on soil retention shown in Figure 6 can be attributed to an electrostatic effect is not known. Snell et al. [24] regard electrostatic force as one of the important factors in the mechanism of soil retention by textile materials, whereas the AATCC Committee [23], while agreeing that such forces do play a part, feel that the evidence is not sufficient to warrant definite conclusions regarding the importance of that part.

Oil Bonding

It has been shown [3, 7, 22, 23] that oil bonding is an important factor in the soiling of textile fibers, particularly in the case of carpet yarns. Fortess and Kip [7] have concluded that the excessive soiling of acetate carpets may be attributed very largely to the presence of oil, and that the acetate fiber is intrinsically soil resistant.

In the present work the influence of oil bonding was presumably eliminated by solvent extraction of the yarn prior to use. However in some of the preliminary work with wool and viscose rayon the yarns were used as received, without preliminary extraction. Comparison of these data with those obtained on the same yarns after solvent extraction (Table IV), illustrates very clearly the marked effect of oil bonding on the soil retention of these yarns. Prior to extraction the wool contained 1.89% extractable matter and the viscose 0.36%. Even the comparatively small amount of oily material in the viscose was sufficient to increase very considerably the soil retention of this fiber.

In the soiling of carpets the influence of oil bonding may be more or less pronounced, depending on whether or not oil present in the backing yarns can

TABLE IV. Effect on Soil Retention of Oily Material in the Yarn

	Wool, W_1				Viscose Rayon, V_1			
Soiling level	0.5	1.0	1.5	2.0	0.5	1.0	1.5	2.0
Effective soil content, original yarn	0.28	0.44	0.62	0.73	0.18	0.24	0.37	0.46
Effective soil content, extracted yarn	0.09	0.16	0.22	0.28	0.09	0.14	0.20	0.25
Increase in soil retention due to oil in yarn, %	200	175	183	160	100	68	85	87

TABLE V. Effect on Soil Retention of Oily Material in the Soil

	Nylon			Acetate		
Relative humidity (%)	0	65	95	0	65	95
Effective soil content, with original soil	0.39	0.17	0.16	0.23	0.13	0.12
Effective soil content, with extracted soil	0.37	0.17	0.16	0.28	0.13	0.15

migrate to the pile fibers from the backing material. Where jute yarns are used in the backing these usually contain an appreciable amount of oil. Fortess and Kip [7] have shown that viscose rayon and acetate yarns transport oil readily while wool and nylon do not. It is probable that this accounts largely for the excessive soiling of some viscose and acetate carpets, as compared with woolen carpets, since the present work indicates that intrinsically wool soils more readily than acetate or viscose rayon.

The influence on soil retention of oily material contained in the soil was also investigated. The soil used throughout the preceding work contained 7.9% of ether-soluble material. A portion of this soil was extracted with ether, dried at 105°C, and conditioned. Soiling tests were carried out with this soil on acetate and nylon yarns which had been conditioned at various relative humidities, as described in the section dealing with moisture content. The results are given in Table V. It is apparent that the oil content of the soil has little, if any, influence on the soil retention of these particular yarns. This is surprising in view of the known effect of oil bonding on soil retention. It might be expected that the effect of oil bonding would be similar whether the oil was initially on the fiber or on the soil.

While some of the factors that contribute to the soiling of textile fibers have been discussed in the preceding sections, others remain to be considered. Thus, while fiber diameter and cross-sectional shape have been shown to influence soiling [18], these factors have not been considered in the present work. Their contribution to a complete picture of the soiling process is recognized, however, and work is now being directed toward a study of these factors.

Acknowledgment

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Some Chemically Modified Celluloses and Their Resistance to Fungal Degradation

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Abstract

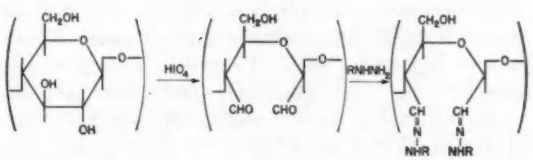
Cellulose has been chemically modified by partial oxidation with periodic acid followed by coupling with various carbonyl reagents.

The modified celluloses have been tested for their resistance to fungal degradation, and some have been shown to inhibit growth at relatively low degrees of substitution (D.S.). The most effective substituent tested was phenylhydrazine, which confers complete resistance to the growth of *Memnoniella echinata* at a D.S. of 0.37%. Some aspects of the inhibitory mechanism and the suitability of the method as a fungus-proofing procedure are discussed.

Introduction

Chemical modification of cellulose has long been known to increase its resistance to attack by fungi. In particular it has been shown by numerous workers that the acetylation of cellulose confers almost complete protection when the degree of substitution (D.S.) is high. Siu and coworkers [6] consider that complete protection is obtained only when each anhydroglucose residue is substituted, the precise nature of the substituent groups being of minor importance.

In the present study, cellulose was modified by the method used by Jermyn and Thomas [2, 3] to produce basic papers for paper electrophoresis experiments. This consists of partial oxidation with periodic acid and coupling of the resulting dialdehyde groups with hydrazine and other reagents. The



choice of substituent groups was largely empirical, the object being to determine which type of compound conferred maximum protection against fungus attack.

Method

Strips of unbleached 12-oz cotton duck were thoroughly wetted by immersion in hot water containing a detergent, and then rinsed; and the excess water was removed by wringing. The duck was oxidized at 28°C for varying periods with aqueous periodic acid solution in a glass tank placed on a reciprocating shaker. The oxidized duck strips were thoroughly rinsed, wrung out, and coupled with the desired reagent. After coupling, the strips were rinsed initially in hot water, then overnight in cold water, and allowed to dry before testing for fungus resistance. The modified cotton duck was tested in parallel with samples of unoxidized but coupled duck and duck in which both the oxidation and coupling steps were omitted. The coupling reagents and experimental conditions are listed in Table I. Nitrogen and (in the case of rhodanine) sulfur analyses of the modified duck were carried out by W. Zimmerman,[1] and these data were used to estimate the per cent D.S., i.e., the number of substituent groups per anhydroglucose residue X 100.

The fungus-resistance tests were carried out by W. R. Hindson[2] and consisted of determining the breaking strength (pounds per inch width) before and after 14 days' incubation with the cellulolytic

[1] C.S.I.R.O., Microanalytical Section, University of Melbourne.

[2] Defense Standards Laboratories, Melbourne.

TABLE I. Methods Employed in the Chemical Modification of Cotton Duck *

Reagent	Experimental Conditions
1. Girard's P reagent (pyridinium acethydrazide chloride)	10% solution in ethanol-acetic acid mixture (90% v/v) at 70°C for 1 hr
2. Hydrazine hydrate	1% w/w aqueous solution at 80°C for 1 hr
3. Semicarbazide hydrochloride	2% aqueous solution+anhyd. sodium acetate (3%) at 80°C for 1 hr
4. Hydroxylamine hydrochloride	2% aqueous solution+anhyd. sodium acetate (3%) at 80°C for 1 hr
5. Phenylhydrazine hydrochloride	1% aqueous solution+anhyd. sodium acetate (2.5%) at 80°C for 1 hr
6. Phenylhydrazine-*p*-sulfonic acid	2% aqueous solution at 80°C for 1 hr
7. Rhodanine (thiazolid-4-one-2-thione)	2% aqueous solution+ammonium chloride (1%)+conc. ammonia (1% v/v) at 80°C for 1 hr

* Percentage concentrations are given as w/v except where otherwise stated.

mold *Memnoniella echinata* under optimum growth conditions. The values given in Table II are the mean of triplicate tests.

In some tests, because of the simultaneous oxidation of a large number of strips, a significant percentage of the periodic acid was reduced so that the concentration gradually decreased during oxidation. Consequently, comparison of the oxidation times and breaking strengths between the different series is not always justified.

The resistance of phenylhydrazine-substituted cellulose to fungal cellulases was investigated using a concentrated culture filtrate of the mold *Stachybotrys atra*.[3] The substituted celluloses consisted of the duck samples listed in Series 5 of Table II and two corresponding series prepared from 0.01 *M* and 0.1 *M* periodic acid oxidized strips of Whatman No. 3 MM filter paper.

The duck samples were ground in a Wiley mill and thoroughly wetted by suspending in water and agitating in a Waring Blendor. Aliquots (2 ml) were then shaken with the enzyme solution (5 ml) in *p*H 5 McIlvaine buffer (5 ml) at 37°C for 18 hr. The extent of hydrolysis was estimated by the production of soluble reducing sugar as determined by the Nelson-Somogyi colorimetric method. However, no enzymic hydrolysis could be detected even in the case of untreated cotton duck.

[3] The production and properties of *S. atra* cellulase will be described elsewhere.

The modified filter papers were ground in a Wiley mill and 100-mg samples shaken with a mixture of enzyme solution (3 ml) and *p*H 5 McIlvaine buffer (3 ml) at 37°C for 3 hr. An identical series of solutions was maintained at 2°C throughout this period, and the enzyme activities were estimated from the difference in soluble reducing sugar contents. All the filter paper samples were susceptible to enzymic hydrolysis, but there was no significant variation in the digestion and hence the cellulase activity was not inhibited by any of the modified celluloses. The D.S. values of the modified filter papers ranged from 0 to 1.94%.

Discussion

From the results in Table II, it can be seen that the nature of the substituent group exerts a considerable influence on the fungal resistance of the cellulose derivative. Thus, while Girard's P reagent, rhodanine, and phenylhydrazine-*p*-sulfonic acid were only slightly inhibitory, the other substituent groups listed, including such small molecules as hydrazine and hydroxylamine, conferred considerable resistance at relatively low degrees of substitution. The most active inhibitor investigated was phenylhydrazine, which at a D.S. value of 0.37% completely inhibited the growth of *Memnoniella echinata* on cotton duck. This corresponds approximately to 1 substituent group per 270 anhydroglucose units.

It follows that the chemical modification of cellulose can confer fungal resistance at surprisingly low degrees of substitution. However, there is no obvious correlation between the amount of protection conferred and either the chemical nature of the substituent group or the D.S. The mechanism of inhibition is obscure; if it is assumed that hydrolysis is effected by an extracellular cellulase, it is improbable that the length of such an enzyme would exceed 270 anhydroglucose units. The only data available on the dimensions of a purified cellulase [8] indicate that it is capable of spanning approximately 20 cellobiose repeating units. However, it is generally accepted that both chemical substitution and enzymic hydrolysis occur more readily in the amorphous regions of the fiber [1]. Thus in the case of cotton duck, which is largely crystalline, the D.S. of the amorphous regions would be much greater and might correspond more closely to the probable dimensions of the enzyme.

In experiments designed to investigate the corre-

TABLE II. Results of Chemical Modification Experiments

Oxidation Time (min)	Coupling Reagent	D.S. (%)	Breaking Strength (lb per in. width)		Visual Assessment of Growth*
			Initial	Residual	
		Series 1 †			
Nil	None	Nil	132	0	+++++
Nil	Girard's P	Nil	144	0	++++
30	Girard's P	—	64	1	++
60	Girard's P	—	44	2	+
		Series 2 †			
Nil	None	Nil	131	0	+++++
30	None	Nil	93	5	+++++
Nil	Hydrazine	Nil	129	1	++++
30	Hydrazine	0.17	73	42	++
Nil	Semicarbazide	Nil	130	1	+++++
30	Semicarbazide	0.42	79	32	++
Nil	Hydroxylamine	Nil	116	3	+++++
30	Hydroxylamine	0.91	83	56	+
		Series 3 †			
Nil	None	0	139	0	+++++
17	None	0	105	4	+++++
17	Phenylhydrazine	0.20	66	65	Nil
17	Phenylhydrazine-*p*-sulphonic acid	0.14	72	3	++
17	Rhodanine	0.20	75	8	++
		Series 4 †			
Nil	None	Nil	125	0	+++++
Nil	Hydrazine	Nil	144	1	+++++
10	Hydrazine	0.09	114	7	++
20	Hydrazine	0.11	97	32	+
30	Hydrazine	0.17	89	36	+
Nil	Phenylhydrazine	Nil	131	1	+++++
10	Phenylhydrazine	0.40	87	85	Nil
20	Phenylhydrazine	0.71	65	65	Nil
30	Phenylhydrazine	0.83	55	50	Nil
		Series 5 ‡			
Nil	None	Nil	127	4	+++++
Nil	Phenylhydrazine	Nil	132	12	+++
10	Phenylhydrazine	0.09	123	39	+++
20	Phenylhydrazine	0.14	115	80	++
30	Phenylhydrazine	0.17	113	88	+
60	Phenylhydrazine	0.23	102	91	Nil
120	Phenylhydrazine	0.37	78	79	Nil

* *Growth key:* +++++ vigorous; ++++ moderate to vigorous; +++ moderate; ++ slight; + very slight.
† Oxidized with 0.1 *M* periodic acid.
‡ Oxidized with 0.01 *M* periodic acid.

lation between the fungal resistance of phenylhydrazine-substituted duck and the inhibition of a cell-free cellulase concentrate, no enzymic hydrolysis of either normal or substituted duck could be detected. At the same time, this enzyme preparation readily hydrolyzed normal and modified filter paper, but no inhibition was observed even at a D.S. value of 1.94%. This comparative resistance of native cotton has been noted previously [7] and may be due to the high degree of crystallinity.

An alternative explanation would be that other essential hydrolysis factors were absent from the cellulase concentrate, for example, the Marsh swelling factor [4]. This *S* factor promotes the swelling of cellulose prior to hydrolysis by other components of the cellulase complex, and it is thought to be an

adaptive enzyme. The cellulase concentrate used in the present experiments was obtained from a culture of *S. atra* grown on a cellulose powder, probably of low crystallinity. In accordance with the results of Marsh et al., the amount of *S* factor produced would be less than from a medium containing native cotton. This could explain the inability of the cellulase preparation to hydrolyze the untreated duck. If this hypothesis is correct, then it follows that the fungal resistance of the substituted duck may be due to inhibition of the *S* factor rather than the other cellulase components.

It seems likely that the controlled production of substituted celluloses will be of value in studies on the mechanism of action of cellulase. From the viewpoint of a fungus-proofing procedure, phenylhydrazine-substituted cotton has the disadvantage that it yields a yellow-colored fabric. A more serious objection to the general method lies in the inherent reduction in breaking strength due to periodic acid oxidation. Some means of offsetting these defects may be summarized as follows:

1. A colorless substituent group of greater inhibitory power than phenylhydrazine might be found which would confer fungal resistance at a D.S. where the reduction in breaking strength due to oxidation was negligible.

2. An inhibitory substituent which could also crosslink adjacent cellulose chains might restore the breaking strength to an acceptable value.

3. A specific oxidation of the anhydroglucose residues of cellulose at carbon atoms 2, 3, or 6 could produce the necessary carbonyl groups without the ring fission and subsequent loss in breaking strength characteristic of periodic acid oxidation. It is possible that the coupling of phenylhydrazine derivatives directly to the hydroxyl groups of unoxidized cellulose might be equally effective.

4. From the results in Table II it can be seen that not all the reagents coupled to the same extent and that possibly the efficiency of phenylhydrazine coupling is less than the attainable maximum. This may be due to the inaccessibility of some regions of the cellulose to certain reagents or perhaps to the oxidation of some aldehyde groups to carboxyl groups during the coupling procedure. By a careful examination of the conditions of coupling it might be possible to increase the degree of substitution relative to the breaking strength.

5. From Series 2 and 3 (Table II) it is apparent that, in addition to the reduction in breaking strength due to periodic acid oxidation, there is a further drop due to coupling with the various reagents. This is probably due to a decrease in the crystallinity of the cotton. Segal and coworkers [5] have shown that anhydrous ethylamine effects a rapid reduction in the crystallinity of cotton cellulose. The conditions of oxidation and coupling which minimize the decrease in crystallinity would therefore yield a stronger fabric. This factor is also important in view of the dependence of fungal resistance on both degree of substitution and crystallinity.

Acknowledgment

The author is grateful to Dr. M. A. Jermyn for much helpful discussion. Thanks are due to Mr. W. R. Hindson for carrying out the fungal-resistance tests and to Mr. G. C. Hawkes for technical assistance.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

The Effect of Voltage and Time on the Electrical Resistance of Cotton

UNIVERSITY OF MANCHESTER
College of Technology
Manchester, England
January 24, 1955

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a recent paper, Hersh and Montgomery [3] found cotton yarn to be ohmic in the range from 50–2000 v. This is in apparent contradiction to the results of various workers, notably Evershed [1], Murphy [4], and Hearle [2], who found that the resistance of cotton decreased as the voltage increased. The results in the literature for other fibers—nylon, wool, hair, and acetate—which Hersh and Montgomery also found to be ohmic, are less conclusive, although Hearle found that the resistance of acetate and, under some conditions, wool decreased as the voltage increased.

We have now carried out an investigation of the reasons for Hersh and Montgomery's apparently anomalous results. As it can conveniently be used over a wide range of voltages, Hersh and Montgomery's circuit was adopted. Dry batteries were used as the source of voltage. The error in determining the ratio of voltages was estimated to be less than 1.5%. For most of the tests a standard resistance of 10^7 ohms was used; this was checked by comparison with a wire-wound 10^6-ohm resistor and found to vary by less than 1% over the range of 10–100 v which occurs on that side of the circuit. For the tests of the boiled cotton yarn, a standard resistance of 10^9 ohms was used; this was not checked for ohmicity but was stated to have a voltage coefficient not greater than 0.02% per volt.

In preliminary experiments, described below, it was found that the resistance values were affected by the time of application of the voltage. In practice a measurement could be made in 3 to 4 sec. At 64% relative humidity, it was estimated that the effect of time would then be negligible up to 500 v, but would cause an increase of resistance of about 3% at 1000 v. Fresh specimens were used for each test, so that there would be no effect due to a previous application of voltage.

The tests were carried out at 64% relative humidity and 20°C, using specimens approximately 1 cm long. The electrodes used were either tin electrodes, as used by Hearle, or brass electrodes coated with silver paint (Duco 4817), as used by Hersh and Montgomery. The yarn was 9s. gray Texas cotton yarn and was tested as received and after boiling in 3 changes of distilled water for 1 hr.

The results of the experiments are shown in Figures 1, 2, and 3, in which the ratio, R/R_{100}, of the resistance to the resistance at 100 v is plotted against voltage. The results for gray yarn, with tin electrodes, between 100 and 400 v are in close agreement with Hearle's results under the same conditions, and none of the experiments show the resistance to be ohmic over the range tested.

In an attempt to find an explanation of the ohmicity in the results obtained by Hersh and Montgomery, we may look at their experimental conditions, which were as follows:

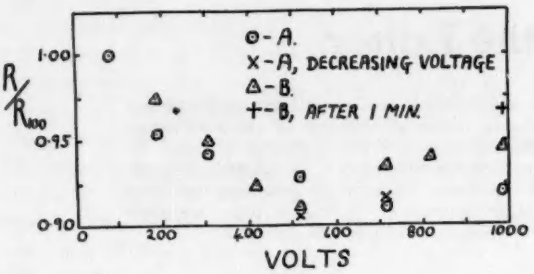

Fig. 1. Effect of voltage. Gray cotton yarn. Tin electrodes. Specimen lengths: *A*, 1.26 cm; *B*, 1.15 cm.

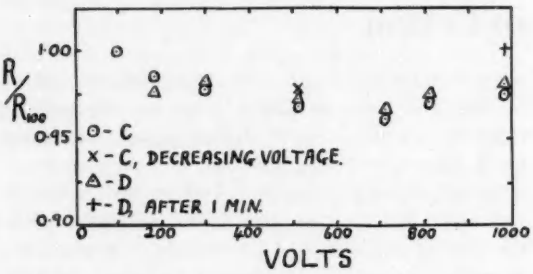

Fig. 2. Effect of voltage. Gray cotton yarn. Brass and silver paint electrodes. Specimen lengths: *C*, 0.9 cm; *D*, 1.05 cm.

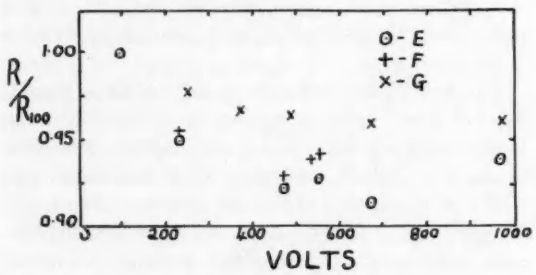

Fig. 3. Effect of voltage. Boiled yarn. Tin electrodes. Specimen lengths: *E*, *F*, and *G*, 0.8 cm.

Relative humidity, 62%. This was near the value of 64% used in the present tests and within the range in which Hearle and Murphy found the effect.

Temperature, 30°C. This is higher than that used in the present tests (20°C), or by Hearle (20°C), or by Murphy (25°C), but this would not be expected to do more than cause some change in the numerical magnitude of the effect.

Test-Length, 2 cm. The present experiments used a 1-cm length, but Hearle found the effect over lengths between 0.2 cm and 12.9 cm, though to a reduced extent as the length increased.

Purity, yarn washed for 3 min each in 3 changes of distilled water. Murphy found that specimens of low electrolyte content had a smaller voltage effect, and this is also shown by the present tests on boiled yarns. The washing treatment used by Hersh and Montgomery could therefore have contributed to the reduction of the voltage effect.

Electrodes, brass and silver paint. In the present tests the voltage effect with these electrodes was found to be about half that found for tin electrodes.

Time of application of voltage, "at least 30 sec, and usually several minutes." The present tests indicate that the resistance increases with time, and thus a reduction in resistance due to a voltage effect might be masked by an increased resistance due to the time effect. This is shown, for example, in Figure 2,

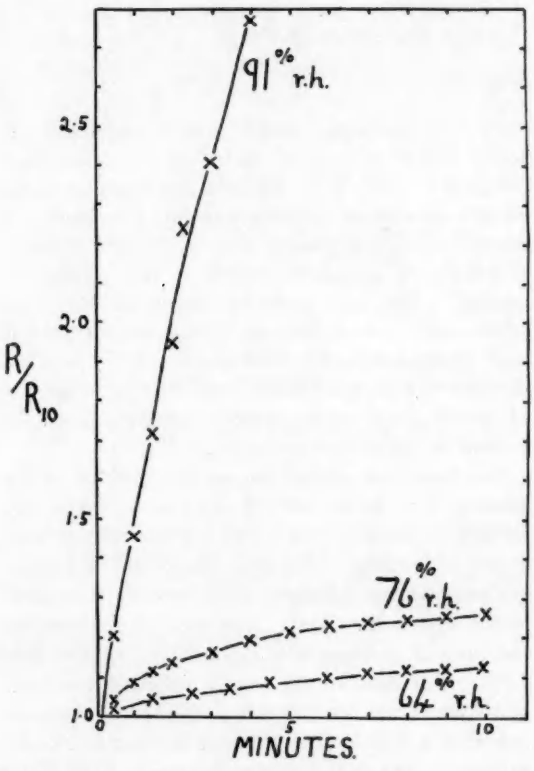

Fig. 4. Effect of time on gray cotton. 1000 v. Tin electrodes. Specimen length, 0.8 cm.

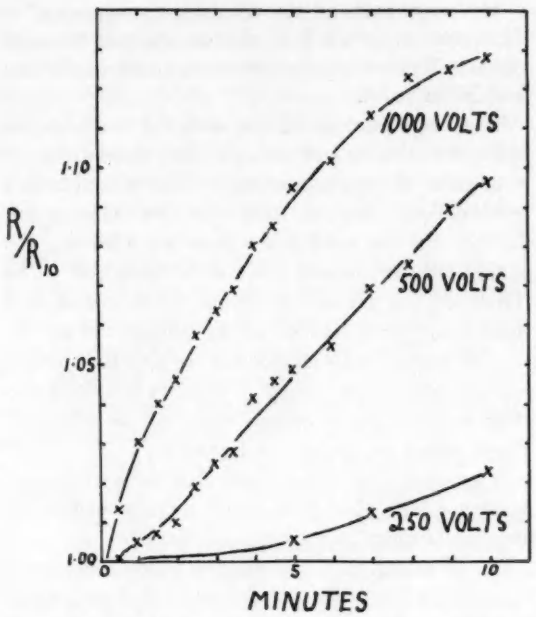

Fig. 5. Effect of time on gray cotton. 64% R.H. Tin electrodes. Specimen lengths, 0.8 cm.

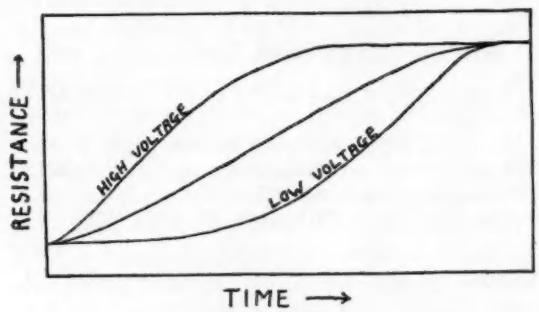

Fig. 6. Family of curves.

where the resistance after 1 min at 1000 v has reached the same value as the resistance at 100 v.

However, the results given below, admittedly at a lower temperature, indicate that equilibrium would not have been attained at all voltages even in several minutes. It would thus appear to be more likely to be fortuitous than to be fundamental for the resistance to appear exactly ohmic. It is probably better to regard the two effects as separate—a decrease of resistance with voltage and an increase of resistance with time—though, in experimental practice, they cannot be completely separated.

Range tested, 50 to 2000 v. In fact, Hersh and Montgomery give results at 50, 75, and 100 v, and then at 100-v intervals from 400–2000 v. Thus the range from 100–400 v, where the voltage effect can be observed with least interference from the time effect, was omitted. (The value at 400 v is between 5 and 10% below the straight line on their plot.)

We may thus conclude that, while other factors may influence results, the ohmicity obtained by Hersh and Montgomery was mainly due, as they

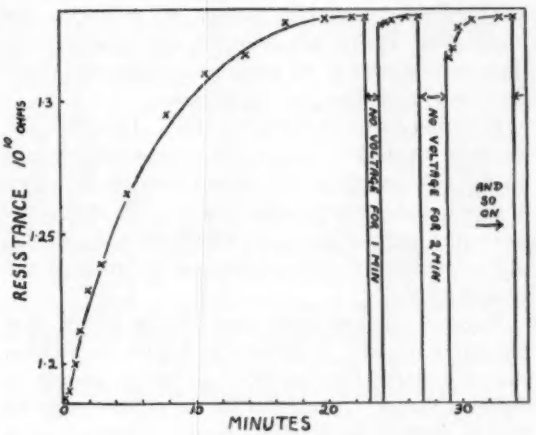

Fig. 7. Effect of time; investigation of recovery. Gray cotton yarn. Tin electrodes. 64% R.H. 1000 v. Specimen length, 0.8 cm.

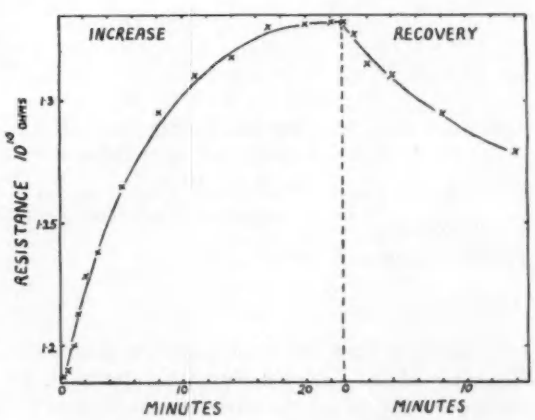

Fig. 8. Effect of time; increase and recovery.

TABLE

Electrodes	R.H. (%)	Volts	Percentage Increase in Resistance: 10 Sec–1 Min	Percentage Increase in Resistance: 10 Sec–10 Min
Tin		250	0.1	2.3
	64	500	0.5	9.8
		1000	2.9	12.9
	76	1000	8.5	26.5
	91	1000	50.0	477
Silver paint	64	1000	2.6	8.7
Tin (boiled yarn)	64	1000	4.2	18.8

suggested, to the length of time for which the voltage was applied, taking into account the voltages used in the test. We cannot, however, feel confident that their results refer to an equilibrium state and therefore have a fundamental significance.

Experiments on the effect of time. In addition to the light which they shed on the experimental results on the voltage effect, the experiments on the effect of time are of interest in themselves. The results are given in Figures 4 and 5, in which the ratio, R/R_{10}, of the resistance to the resistance at 10 sec is plotted against time.

Figure 4 confirms what was found by Hearle, that the effect of time is greater at higher humidities. Figure 5 shows that the effect of time is greater at higher voltages. The form of the curves suggests that they might be part of a family of curves, as in Figure 6, and that, whereas at 1000 v the resistance would be near equilibrium after 10 min, at lower voltages equilibrium would be reached much more slowly.

The magnitudes of the effects are summarized in the Table, in which it is also shown that the time effect is somewhat less with brass electrodes coated with silver paint.

Tests were also carried out, with the results shown in Figure 7, to see how the resistance recovered after removal of the applied voltage. The resistance had reached equilibrium at 1000 v at 64% relative humidity, and the resistance values after leaving the voltage off for various times were measured. The resistance was allowed to return to its equilibrium value before each removal of the voltage. If the resistance curves are extrapolated back to the time of reapplication of the voltage, a value of the resistance after recovery for a certain time can be obtained. These values are plotted in Figure 8.

It appears from these results that the variation of resistance with time is in many ways analogous to mechanical creep and recovery behavior.

One of us (G. E. C.) is grateful to the Electors of Courtauld's Scientific and Educational Trust Fund for the award of a Research Scholarship.

G. E. CUSICK
J. W. S. HEARLE

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TEXTILE RESEARCH INSTITUTE
Princeton, New Jersey
March 21, 1955

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

We wish to thank Mr. Cusick and Dr. Hearle and the editor of the TEXTILE RESEARCH JOURNAL for the opportunity to see the above communication [1] before publication. In essence we are in agreement with Cusick and Hearle as to the likely explanation of the effects noted by them and by us. In particular, we are gratified to see that their cotton sample mounted on silver-painted brass electrodes was ohmic within 3% over all the conditions reported, and that after the 1000 v potential was applied for 1 min (conditions comparable with those of our measurements), the cotton indeed appeared to be ohmic. But whether this result is fortuitous or not is still uncertain.

In our paper [3] we stated (p. 809) that all the samples examined were free of time effects except that "With low resistances, of the order of 10^{10} ohms, an increase in resistance with time was observed; it

is believed that this increase results from loss of moisture through heating." For most of the work reported there, the resistance was above 10^{10} ohms. In particular, for the 21's cotton yarn at 30° C and 64% R.H., the resistance was 25×10^{10} ohms. Although Cusick and Hearle do not give numerical values for their resistances, we conclude from their values of applied voltages (100–1000 v), the measured voltages (10–100 v), and standard resistance (10^9 ohms) that the resistance of the samples of boiled cotton yarn was about 10^{10} ohms, corresponding to resistivities of 10^8 ohm-cm. Thus, there is no immediate inconsistency in our results, since we too observed time-dependent effects with cotton yarns having such low resistances (although we reported no quantitative results on such yarns).

However, we believe that there is a real point here. The apparatus as used for these measurements is a kind of hot-wire anemometer, and unless heat is lost quite rapidly from the filament, the measurements at different voltages or times are not isothermal. This effect is usually negligible with high-resistance materials, but with better conductors (resistances of 10^{10} ohms or less) it may become appreciable. We have tried to estimate this effect for various experimental conditions, and find (1) the heat input per unit mass of sample is sufficient nearly to attain temperature equilibrium within the waiting periods employed in making the measurements; (2) there can be a significant temperature rise at equilibrium, which we estimate for the Cusick and Hearle boiled sample to be about 0.01°C times $(V_x/100)^2$, where V_x is the voltage drop across a 1-cm sample, and for the Hersh and Montgomery case about $\frac{1}{5}$ to $\frac{1}{10}$ that value; (3) it is reasonable that such temperature rises are large enough to account for the nonohmicity observed by Cusick and Hearle at 65% R.H. (1°C at 1000 v/cm, to give a 10% decrease in resistance [2]) and yet not so large as to rule out the ohmicity observed by Hersh and Montgomery at about the same humidity (0.1–0.2°C at 1000 v/cm, to give a 1–2% decrease in resistance); (4) with longer times of application of voltage, the sample will lose moisture to reach the steady-state regain that corresponds to the lower relative humidity determined by the absolute moisture content at the chamber temperature relative to the saturation content at the increased sample temperature. This will cause an increase in resistance with time, and the total increase will be greater the greater the voltage across the sample and the greater the relative humidity. Of course, as the fiber dries out and its resistance increases the heat input will be lowered. However, this should be a secondary effect. Presumably such behavior would be in part an explanation of the results given by Cusick and Hearle in Figures 4 and 5 and also of the results shown in their Figures 7 and 8.

If this conjecture is to prove true (and if indeed cotton is ohmic), then the nonohmicity would become less as the sample diameter is decreased and as the air velocity in the chamber is increased, for the same range of voltage gradient across the sample. A further test would be that suggested by Figure 6 of Cusick and Hearle; at vanishing temperature rise the curves should coalesce to a horizontal line (apart from possible long-time effects due to depletion of charge carriers), and, at nonvanishing rises, the curves would reach limiting values whose magnitude would increase as the applied voltage increased.

S. P. HERSH [1]
D. J. MONTGOMERY [2]

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Tetra-*O*-Methyl-D-Glucopyranose from *O*-Methylcellulose

BRITISH RAYON RESEARCH ASSOCIATION
Heald Green Laboratories
Wythenshawe, Manchester, England
February 22, 1955

To the Editor,
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a recent paper "The Distribution of Methoxyl Groups in Partly Methylated Cellulose" [1] L. Rebenfeld and E. Pacsu note the absence of tetra-*o*-methyl-D-glucopyranose in hydrolysates of *o*-methylcelluloses. They comment "(The) presence of (tetramethylglucose) would be expected from highly methylated cellulose on the basis of the classical structure. This absence of tetramethylglucose, especially from materials of low degree of polymerization, constitutes one of the major unsolved problems in cellulose chemistry."

This is a point of fundamental importance and I wish to bring to your notice a paper "The Detection and Determination of 'End Groups' in *o*-Methylcelluloses" [2]. Hydrolysis of the *o*-methylcelluloses gave tetra-*o*-methyl-D-glucopyranose which was isolated from the hydrolysate, identified, and determined. The degree of agreement observed between the values for the number average degrees of polymerization of the *o*-methylcelluloses in the range 200–1000 determined osmotically and by end-group analysis establishes the validity of the open-chain structure for cellulose.

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D. I. MCGILVRAY

TEXTILE RESEARCH INSTITUTE AND
FRICK CHEMICAL LABORATORY
Princeton, New Jersey
March 19, 1955

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Ever since in 1914 Denham and Woodhouse discovered a trace of tetramethylglucose in the hydrolyzate of their partly methylated cellulose, the presence or absence of this "end group" has become one of the vexing problems in cellulose chemistry. The successful application in carbohydrate chemistry of paper chromatography invited re-examination of the end-group problem, and Dr. McGilvray's article is the first report on the results obtained by the application of this new technique.

Contrary to earlier investigators (Hess, 1937; Haworth, 1939) McGilvray found evidence of the presence of end groups in "natural cellulose" samples, such as American and Egyptian cotton and bleached wood pulp after methylation with the rigorous exclusion of oxygen. After concentration by extraction with light petroleum of any methyl tetramethylglucoside that was present in the aqueous solution of glucosides, McGilvray succeeded in obtaining fractions which contained tetra- and trimethylglucose in the ratio of 1:16.0 and 1:51.7. The D.P. values calculated from end groups showed variations from about 250 to 2340.

In the course of our recent work we had opportunity to examine a large number of chromatograms obtained from methylcellulose and methylhydroviscose, and not once could we find traces of spots that would have suggested the presence of tetramethylglucose. Particularly in the hydrolyzates originating from our low D.P. (52) hydroviscose, where the ratio should be equal to that in one of McGilvray's concentrates, there were no such spots discernible. In view of the fact that in pertinent experiments we had no difficulty in detecting tetramethylglucose in quantities as small as 10 to 15γ, we came to the conclusion that our negative result was in agreement with the findings of earlier investigators. To be sure, in the case of our high D.P. ($\sim$ 900) methylcellulose it is not impossible that the quantity of the hydrolysate put on the paper was

insufficient to reveal the presence of a tetramethylglucose component.

However, the discrepancy between McGilvray's and our results might be attributed to the fact that he did not use the American Chemical Society method for purification but "In order to minimise degradation unscoured cotton was used as the raw material. . . ." Indeed, his ethanol extracts were shown by paper chromatography to contain mannose, glucose, and galactose, together with cellobiose and "higher oligosaccharides." Inasmuch as ethanol is not a good solvent for such impurities, it is entirely possible that some of the higher oligosaccharides remained entrapped in the fibers and survived the methylation treatment and washing operations. If such be the case, then the tetramethylglucose found by McGilvray could have originated from incidental or structural impurities of the type of hemicellulose embedded in his "natural cellulose" samples which had not been submitted to the standard pretreatment with 2% alkali.

McGilvray's finding that the D.P. values derived from the tetramethylglucose "agree with those values obtained physico-chemically" may come as a surprise to those who do not expect an almost perfect agreement between the viscosity D.P. (256–260) and the end-group D.P. (245–244) for cellulose chains degraded in a supposedly random manner. On the other hand, this result, if confirmed, would constitute a powerful argument in favor of the theory of periodically occurring weak bonds in cellulose structure.

Before accepting Dr. McGilvray's results at their face value it would be most desirable, in our opinion, to repeat his experiments by applying his technique to "standard cellulose" instead of "natural cellulose."

E. PACSU [1]
L. REBENFELD [2]

The Effect of Nuclear Radiation on Wool Fiber

NORTH CAROLINA STATE COLLEGE
School of Textiles
Raleigh, North Carolina
March 22, 1955

To The Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In a forthcoming publication, the effect of nuclear radiation (principally neutrons and gamma rays) on the properties of wool will be described. A series of experiments have been conducted in the Raleigh Research Reactor and at the Brookhaven National Laboratories in which the fibers were exposed to different total dosages of radiation ranging from 10^{15} to 10^{18} nvt.

The exposed wools were examined for changes in stress-strain characteristics, alkali solubility, acid-combining capacity, and sulfur, nitrogen, cystine, and tyrosine content. The analytical work completed to date has shown that there was no appreciable effect on the wool up to 10^{16} nvt. At this level, the alkali solubility started to increase, and the stress-strain properties of single fibers showed a significant change. No other effects were noted at 10^{16} nvt. As the dosage was increased beyond this level there was a very sharp rise in solubility in alkali, and at 10^{17} nvt a value of 92% was obtained. At this level the 30% index, determined from stress-strain curves, was 0.31. The cystine content was reduced from 9.4% to 7.6% and the acid-combining capacity changed from 0.80 to 0.64 meq per gram. There was no change in total sulfur or total nitrogen content. At 10^{18} nvt the fibrous characteristics of the wool were totally destroyed.

The 30% index was determined by the procedure developed by Sookne and Harris [2]. In this procedure the stress-strain curve of a single wool fiber to 30% extension is determined; the "calibrated" fiber is then subjected to a treatment and the stress-strain curve redetermined. The 30% index is then defined as the ratio of the work required to extend the fiber 30% after treatment to that required for the same extension before treatment. In the present work, the calibrated fibers were exposed to radiation and the 30% indexes determined. Two things of interest were noted. First, the *shape* of the stress-strain curve of the exposed fiber was identical with that of the unexposed even though at a level as high as 10^{17} nvt only $\frac{1}{3}$ as much energy was required to extend the fiber after exposure as before. Thus, the long-range elastic recovery was not lost.

Second, the change in 30% index brought about by the nuclear radiation was independent of fiber diameter. Identical 30% indexes were obtained on fibers of different deniers at a given level of radiation.

For comparative purposes, one series of wool samples was prepared by treatment with hydrochloric acid solutions of different concentrations and another by treatment with 10-volume hydrogen peroxide for different periods of time. The first treatment was done to determine the effect of hydrolysis on the properties of the wool, and the second to determine the effect of oxidation of the cystine [2].

(An interesting and as yet unexplained observation was made during the course of this work. It was not possible to determine the 30% indices of wool fibers exposed to the H_2O_2 solutions although no difficulty was encountered with the fibers treated in HCl. The calibrated single fibers disentegrated in the H_2O_2 after about 30 min, while the remaining mass of wool fibers in the same beaker withstood the treatment up to 8 hr. Single fibers were selected from the mass of fibers that was treated for 8 hr and their stress-strain properties determined. The characteristic curve for wool was obtained and a considerable retention of strength was observed. No reason for the anomalous behavior of calibrated fibers toward H_2O_2 has been suggested.)

The hydrochloric acid as well as the peroxide treatment resulted in increased solubility of the wool in alkali but the overall results indicated that the effect of hydrogen peroxide was more nearly like that of the nuclear radiation. Thus, it is believed at present that the predominating effect of nuclear radiation on wool, when exposed in an atmosphere containing oxygen and water, is one of oxidation of cystine. The possibility of some cleavage of amide linkages is not excluded.

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ROSA D. KIRBY
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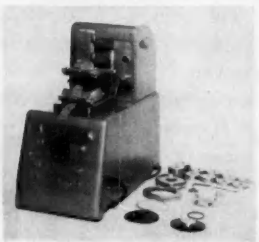

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